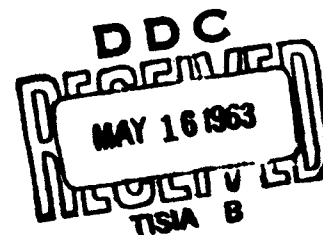65-3-4

ROCKETDYNE

A DIVISION OF NORTH AMERICAN AVIATION. INC.

CANOGA PARK, CALIFORNIA

R-5077

RESEARCH IN FLUORINE CHEMISTRY

· SUMMARY REPORT

(16 March 1962 to 15 March 1963)

ROCKETDYNE

A DIVISION OF NORTH AMERICAN AVIATION. INC.

6633 CANOGA AVENUE
CANOGA PARK, CALIFORNIA

Contract Nonr 1818(00)

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Foreword

The research effort described in this report was conducted by the Synthetic Chemistry Group of the Rocketdyne Research Department. The work was supported by the Office of Naval Research under contract Nonr 1818(00), under the cognizance of Mr. Richard Hanson as Scientific Officer.

This report, which covers the period 16 March 1962 to 15 March 1963, consists of five technical papers and includes work previously published in Rocketdyne reports R-334-18, R-334-19, and R-334-20, as well as work conducted during the final quarter. Since these technical papers, in effect, summarize the entire program in electrochemical synthesis of nitrogen-oxygen-fluorine compounds, some of the results previously published in Rocketdyne Summary Report R-3505 also were drawn upon. Full time associates for this work were Dr. Howard H. Rogers, who was Responsible Scientist, and Julian H. Johnson. Dr. Sheldon Evans of the Physical Chemistry Group contributed the electrochemical interpretations.

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ELECTROLYSES IN ANHYDROUS HYDROGEN FLUORIDE

I. The Drying of Hydrogen Fluoride by Electrolysis

By H. H. Rogers, S. Evans, and J. H. Johnson

Periodically reversing the direction of current in an electrolytic cell has been shown to lead to effective drying of hydrogen fluoride because it causes extensive depolarization. Its obvious advantage is that, by allowing a higher average current to pass, the time required for drying is greatly shortened and, thereby, the attack on the nickel electrode is reduced markedly. The portion of the current used for nickel dissolution was never greater with current reversal than in the conventional procedure where the current was not periodically reversed.

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Introduction

The use of hydrogen fluoride as an electrolyte often requires the removal of water to avoid the formation of unwanted oxygen-containing compounds during electrolysis. In addition, the electrochemical reactivity and properties of non-aqueous solvents are frequently quite different in the presence of even small amounts of water. Methods for producing pure dry hydrogen fluoride which are discussed by Runner, Balog, and Kilpatrick[1], all involve either potassium hydrogen fluoride or sodium (1) hydrogen fluoride as an intermediate. These methods can produce very dry products which are characterized by very low conductivities approaching $10^{-6}ohm^{-1}cm^{-1}$; the values first measured invariably increase to about $10^{-4}ohm^{-1}cm^{-1}$ when the product is permitted to stand for a period of time. The extremely pure product is not generally needed for electro-synthetic work and, in addition, requires considerable time and equipment to prepare. These methods are, therefore, not usually employed for producing dry hydrogen fluoride prior to carrying out electro-synthetic experiments.

Simons[2] states that commercial hydrogen fluoride was dried by pass- (2) ing a current through it until fluorine was evolved. Water was removed as oxygen, oxygen difluoride, and hydrogen. This method was employed by Kongpricha and Clifford[3] who passed current until the conductivity (3) was low and the cell gave a constant back potential for several hours after electrolysis was stopped. Although this electrolytic drying process has been used by other workers[4], no further details of either pro- (4) cedure or of the drying efficiency of the process have been found in the literature.

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The authors' experience with the electrolytic drying process[2] has indicated that hydrogen fluoride cannot be dried satisfactorily in a reasonable length of time, overnight for example, because of severe anodic polarization. On the other hand, if the electrode arrangement provided a very large electrode area (such as in the Simons' Cell[5]) in comparison to the amount of hydrogen fluoride to be dried then it was apparently possible to pass sufficient amounts of current at a <u>low</u> average current density to dry the hydrogen fluoride in one or two days. It should be pointed out that this process is accompanied by severe anode corrosion.

(5)

The results of experiments which contrast the effectiveness of conventional electrolytic drying of hydrogen fluoride[2] with a new procedure, drying by periodic current reversal, will be discussed.

Experimental

The electrolytic cell, Fig. 1, constructed almost entirely of welded (Fig. 1)
stainless steel sheet, was designed for maximum cooling efficiency. Re-
frigerated methanol was circulated through a jacket that completely
surrounded the cell except for the top. The temperature of the electrolyte
was monitored with the aid of a copper-constantan thermocouple inserted
into a stainless steel well which was located between the electrodes
(Fig. 2). Suitable fittings were provided for the addition of liquid (Fig. 2)
hydrogen fluoride (Matheson) directly from the cylinder. A reflux con-
denser, maintained at about $-18°$ by circulating methanol, returned vapor-
ized hydrogen fluoride to the cell.

The sheet nickel electrodes had an area (one side) of approximately
10 x 6 cm exposed to the electrolyte when the cell was filled with 250 ml
of liquid hydrogen fluoride; the useful capacity of the cell was from
40 to 360 ml. The electrodes were mounted on nickel rods, as shown.
These rods were forced into short lengths of Kel-F rods which were, in
turn, forced into the cover of the cell. In each instance, the holes
were drilled very slightly smaller than the diameter of the rod, pro-
viding a vacuum tight seal.

Electrical power was obtained from a Knight Battery Eliminator[6] (6)
connected in series with a current regulator. The circuit was adapted
from known circuits[7-9] and will be submitted for publication elsewhere. (7-9)
The regulator permitted electrolyses to be conducted at constant current
over a current range from 0.001 to 15 amperes. Current, input voltage,
and electrode potential readings were recorded by Rustrak Model A
Recorders connected with the appropriate shunts and multiplier resistors.

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A transistorized automatic reversing switch provided a means for reversing current periodically to the cell during reverse-current drying. An additional set of contacts also reversed connections to the voltage recorder. Although the transistorized switch was continuously adjustable to obtain either equal or unequal time intervals from 1 to 40 seconds, a simple mechanical switch set to reverse connections about every 30 seconds would have been satisfactory.

Current was brought into the electrodes through the nickel support rods. Cell voltage was measured across the other two nickel support rods, thereby virtually eliminating any errors due to a high-resistance connection to one of the electrodes. Electrode potentials were measured between the electrode under study and a platinum wire electrode with a General Radio 1230-A D.C. Amplifier and Electrometer. The platinum electrode in the measuring circuit, where there was negligible current drain, functioned satisfactorily as a poised reference rather than as a nonpolarizable reference electrode.

Additional experimental and procedural details are given below. Details of the operating conditions, typical of those used for electrolysis, are presented in Tables I and II.

Inert gas was used to dilute the gaseous products, thereby reducing the severity of explosions which sometimes occurred during electrolysis. A flow of about 50 cc/min of helium was found to be adequate.

The liquid level in the cell was found by using a probe made from a piece of monel rod covered, except for the ends, with a thin Kel-F sleeve (electrical spaghetti). The probe, inserted into the cell through a Teflon "O" ring, was lowered slowly until it made electrical contact

TABLE I

DETAILS OF ELECTROLYSIS EXPERIMENTS, ELECTRICAL DATA

Run	Reactants	Potentials, Volts	Current, Amperes	Length of Run, hrs.	Reversal Periods, Sec.
1	HF-200 ml	8.0 → 15.4	5.2 → 0.96	1.7	None
2	HF-228 ml	8.0 → 15.0	5.6 → 2.8	6.0	40
3	HF-280 ml	9.6 → 26.8	3.2 → 0.28	20.5	30
4a	HF-216 ml	10 → 23**	6.0 → 0.60**	17.5	40
4b	HF:NH$_3$*	5.3 → 4.8	0.75	2.0	None

Internal Cell Temperature −8 to −16°.

* Mole ratio 15:1

** At end of 6.0 hours

TABLE II

DETAILS OF RESULTS OF ELECTROLYSIS EXPERIMENTS

Run	Weight loss, grams Anode*	Cathode*	Current Equiv. of Wt. loss, amps.	Products Principal	Trace	Current Reversal
1	0.574	0.016	0.32	OF_2	CF_4	No
2	1.023	0.958	0.36	OF_2	CF_4, NO_3F	Yes
3	1.045	0.870	0.086	Not determined		Yes
4a	1.735**	1.371**	0.16	Not determined		Yes
4b				NF_3	CF_4	

Nickel electrodes cleaned with abrasive paper before each run

*or electrode normally acting as anode or cathode

**Total weight loss for Parts a and b

with the electrolyte as indicated by an ohmmeter. Since the depth to which the rod had been lowered was proportional to electrolyte level, not only could the quantity of electrolyte added be determined, but the loss of electrolyte during electrolysis as well.

Results and Discussion

According to Burdon and Tatlow[10], the drying of hydrogen fluoride (10)
by electrolysis causes a reduction in current until the conductivity is
almost zero when complete drying has occurred. If it is assumed that the
current measured is proportional only to the quantity of water in the
system, this amperometric measurement is valid.

Typical current and potential behavior monitored during the conven-
tional electrolytic drying process (without current reversal) is shown
in Fig. 3. In this graph it can be seen that the current did fall off (Fig. 3)
as a function of drying time. However, the resumption of electrolysis
after breaking the circuit resulted in an increased current. This indi-
cated that electrode effects, rather than solution conductance, were the
limiting factor in determining the cell current. Therefore, any strict
interpretation which relates current to solution conductance, i.e.
quantity of water, is not valid under these conditions. In six seperate
experiments hydrogen fluoride was dried in this manner for 2 to 3 hours
prior to the addition of ammonia. Subsequent electrolysis of this
system consistently yielded oxygen difluoride as a product, indicating
that water removal was incomplete. Oxygen difluoride was still produced
during electrolysis when the ammonia was pre-dried over sodium.

In contrast, when the hydrogen fluoride was dried using periodically
reversed current, the current and potentials were unchanged when elec-
trolysis was resumed after a short time interval (Fig. 4). Thus, changes (Fig. 4)
in current and potential observed previously must have been a function
of solution resistance.

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Further confirmation of the cause of this resistance change was obtained from analysis of diagnostic tests (Table III). Electrode potentials were measured at the end of a run between the platinum reference electrode and each of the nickel electrodes, observing the electrode configurations illustrated in Table III. The difference in anode as well as cathode potentials, as measured with both configurations, was caused by the IR drop in the solution. Based on previous results, it was reasonable to assume a real cathode potential of 1 volt (with insignificant IR contribution) and a total solution resistance of about 27 ohms was then calculated. Without any such assumption, however, the solution resistance calculated between the reference electrode and the nickel electrode, which is not in close proximity to it, was 25 ohms. On examination of the values obtained on conventional drying (Table III), it can be seen that there is a negligible contribution of solution resistance to the electrode potential value as measured between the reference electrode and the nickel electrode which is not in proximity to it.

While it is not justifiable to derive any value of specific conductivity from such resistance measurements, it is possible to correlate the observed high solution resistance values with effectiveness of drying. Thus, when ammonia was added to hydrogen fluoride which was dried with the current reversal method, subsequent electrolysis did not yield oxygen difluoride or any oxygen-containing product (Run 4, Tables I and II), indicating that water removal was essentially complete.

The drying of hydrogen fluoride with current reversal is effective because during electrolysis it is possible to pass higher average currents than during conventional drying processes. The variation of

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TABLE III

ELECTRODE POTENTIALS AT END OF TYPICAL RUNS

	Cell Configuration		E Anode	E Cathode
Conventional Drying	C	RA	15	−0.9
Reverse Drying	C	RA	12	−17
Reverse Drying	A	RC	27	−2.3

A = Anode

C = Cathode

R = Platinum reference electrode

Potentials (in volts) listed were measured with respect to reference electrode.

Measured at 0.63 amperes.

applied potential during current reversal is illustrated in Figure 4c.
If it can be assumed that the polarization which occurred during con-
ventional drying was a result of the onset of passivity, then it is
possible that, by reversing the current, the passive film was removed
cathodically, thereby causing gross depolarization. Clearly this is <u>not</u>
the process which occurred. The buildup of passivity is associated with
metal dissolution (to form a passive film some metal must dissolve) so
that the periodic destruction and formation of a passive film must be
accompanied by severe weight loss. The average portion of the current
which assists in the dissolution process, calculated from weight loss
data, is never significantly larger for the current reversal process
than for the conventional process (Table II). The depolarization
observed with the current reversal process is not related to a passive
film, but probably resulted from the obviation of other forms of
polarization, such as concentration polarization or gas-film
polarization.

The additional current which passes with the current reversal
process is related directly to the quantity of water removed and not
to any further metal dissolution. The current reversal technique used
in cells designed specifically for electro-synthesis permits more
effective drying in shorter time periods than the conventional
electrolytic procedure and, therefore, results in considerably less
metal consumption.

Acknowledgments

References

(1) M. E. Runner, G. Balog, and M. Kilpatrick, J. Am. Chem. Soc., 78, 5183-6 (1956).

(2) J. H. Simons, J. Electrochem. Soc. 95, 47-52 (1949).

(3) S. Kongpricha and A. F. Clifford, J. Inorg. Nucl. Chem., 18, 270-5 (1961).

(4) R. D. Dresdner and J. A. Young, J. Am. Chem. Soc., 81, 574-7 (1959).

(5) J. H. Simons, U. S. 2,519,983, Aug. 22, 1950.

(6) Cat. No. 83YX505J, Allied Radio Corporation.

(7) Military Standardization Handbook, "Selected Semiconductor Circuits," MIL-HDBK-215, June 15, 1960, Superintendent of Documents, U. S. Government Printing Office, Washington 25, D. C.

(8) Application Note AN3, "Current Regulator," Minneapolis-Honeywell Regulator Co., Minneapolis 8, Minnesota.

(9) Application Note 4B, "Current Regulator," Delco Radio Division, General Motors Corp., Kokomo, Ind.

(10) J. Burdon and J. C. Tatlow, in M. Stacey, J. C. Tatlow, and A. G. Sharpe, "Advances in Fluorine Chemistry," Vol. I, Academic Press, Inc., New York, 1960, p. 134.
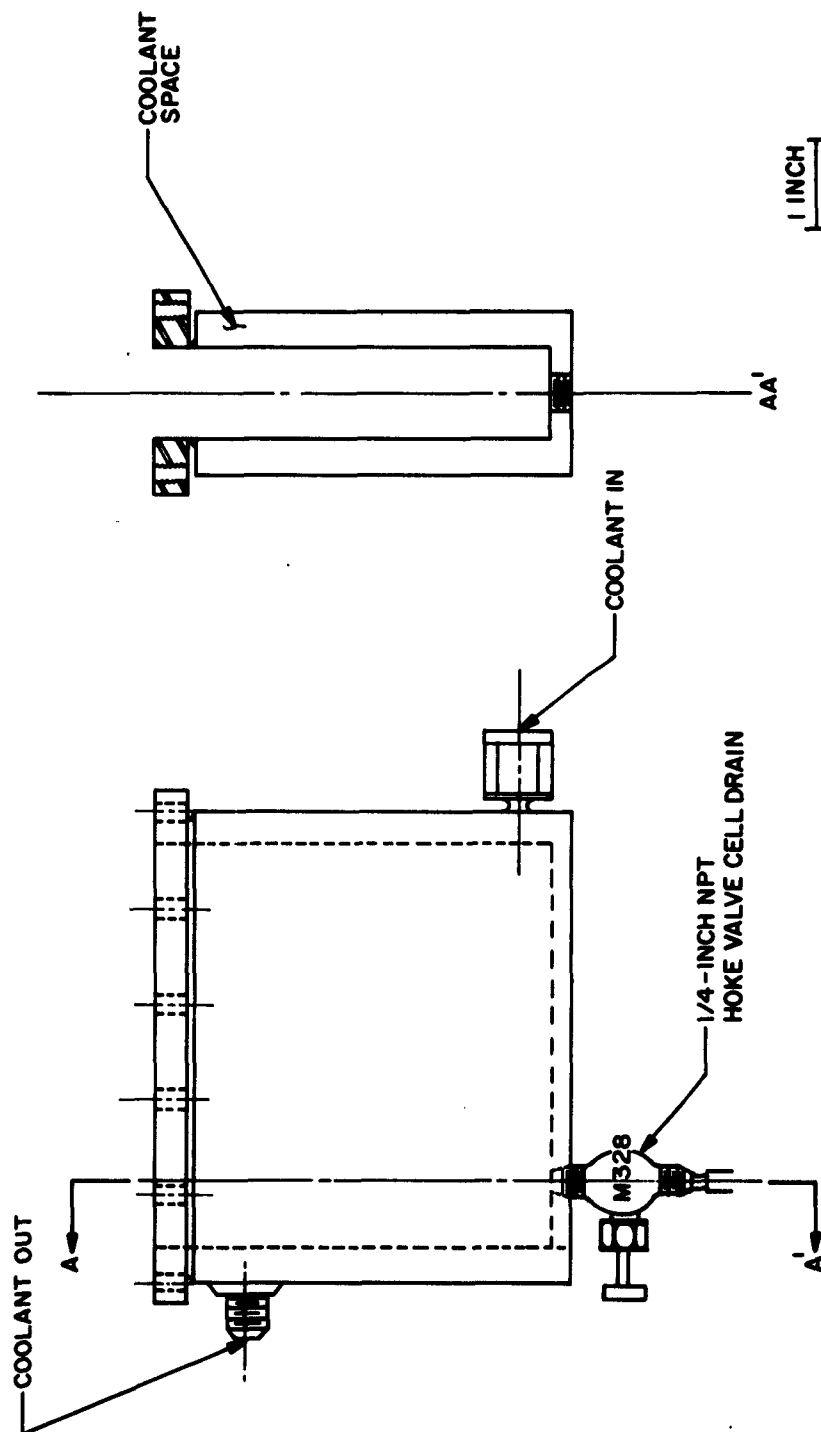
COOLANT SPACE

1 INCH

AA'

COOLANT IN

COOLANT OUT

M328

1/4-INCH NPT
HOKE VALVE CELL DRAIN

A

A'

Figure 1. Electrolytic Cell (Stainless Steel Welded) Electrolysis in Anhydrous
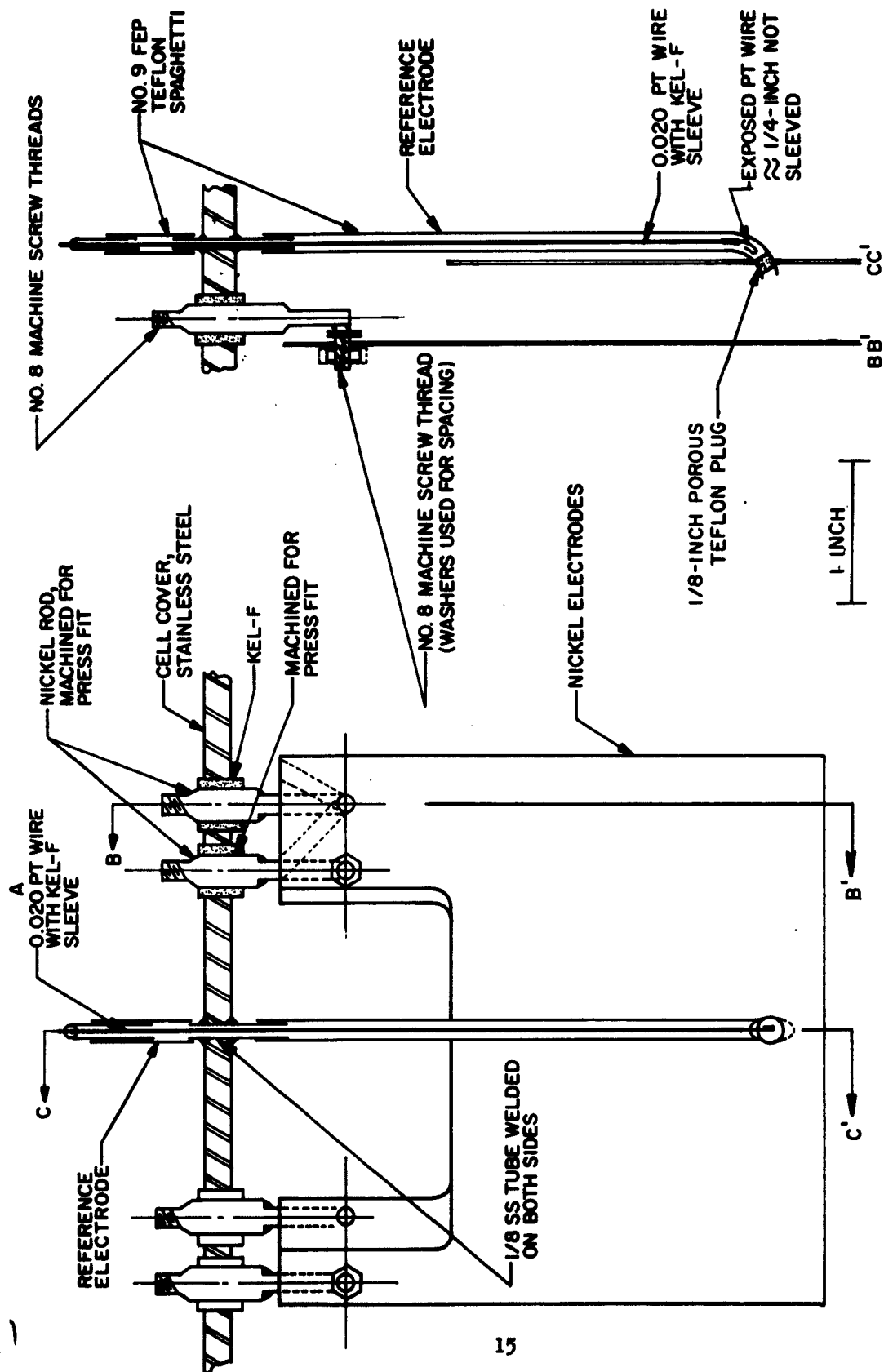Hydrogen Fluoride by H. H. Rogers, S. Evans and J. H. Johnson

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Figure 2. Electrode Assembly Electrolysis in Anhydrous Hydrogen Fluoride by H. H. Rogers, S. Evans and J. H. Johnson
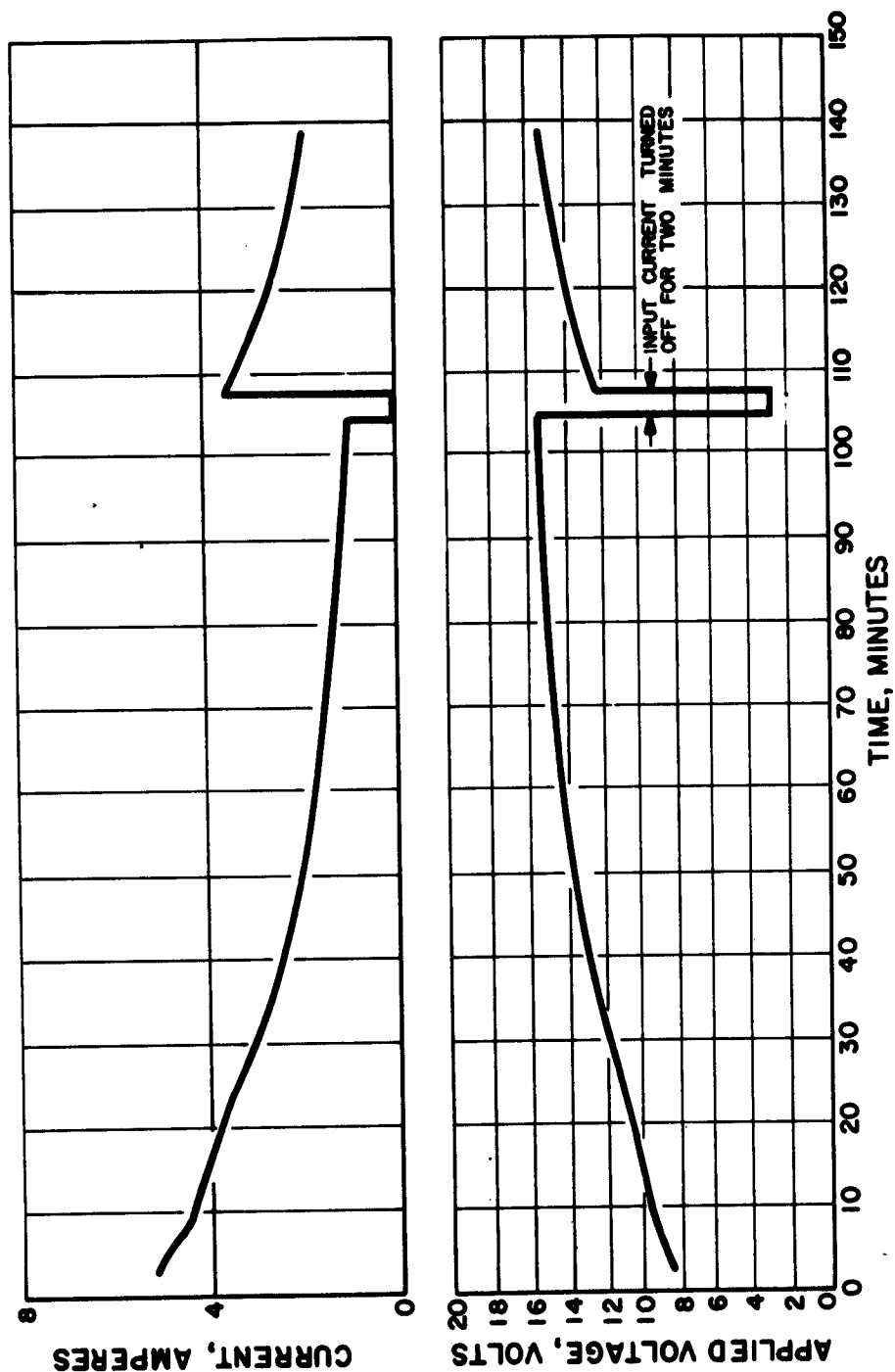
15

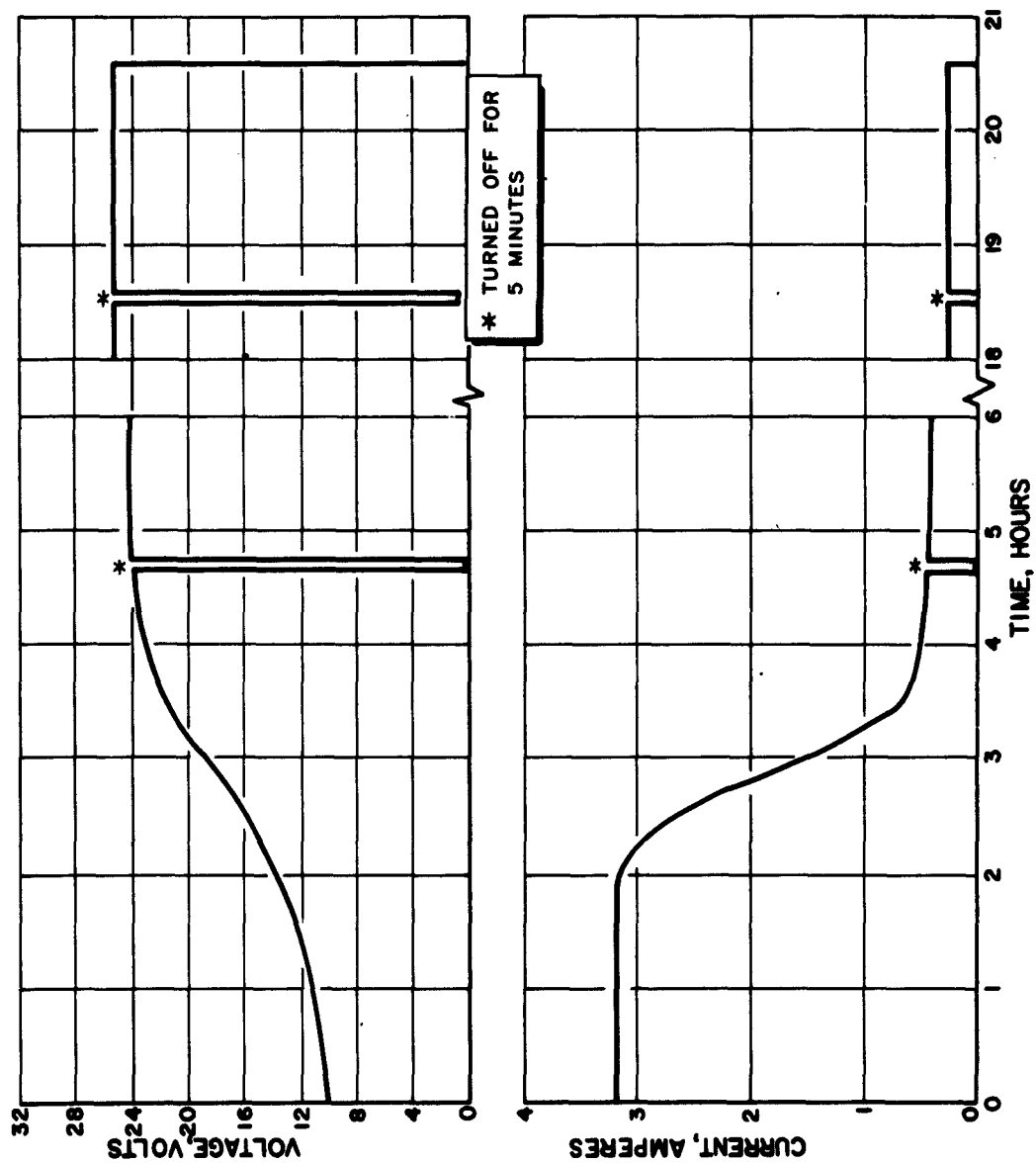Figure 3. Typical Run, Electrolytic Drying of HF Without Reversal

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Figure 4a, b, Typical Run, Electrolytic Drying of HF With Current Reversal

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DETAILS OF VOLTAGE CURVE
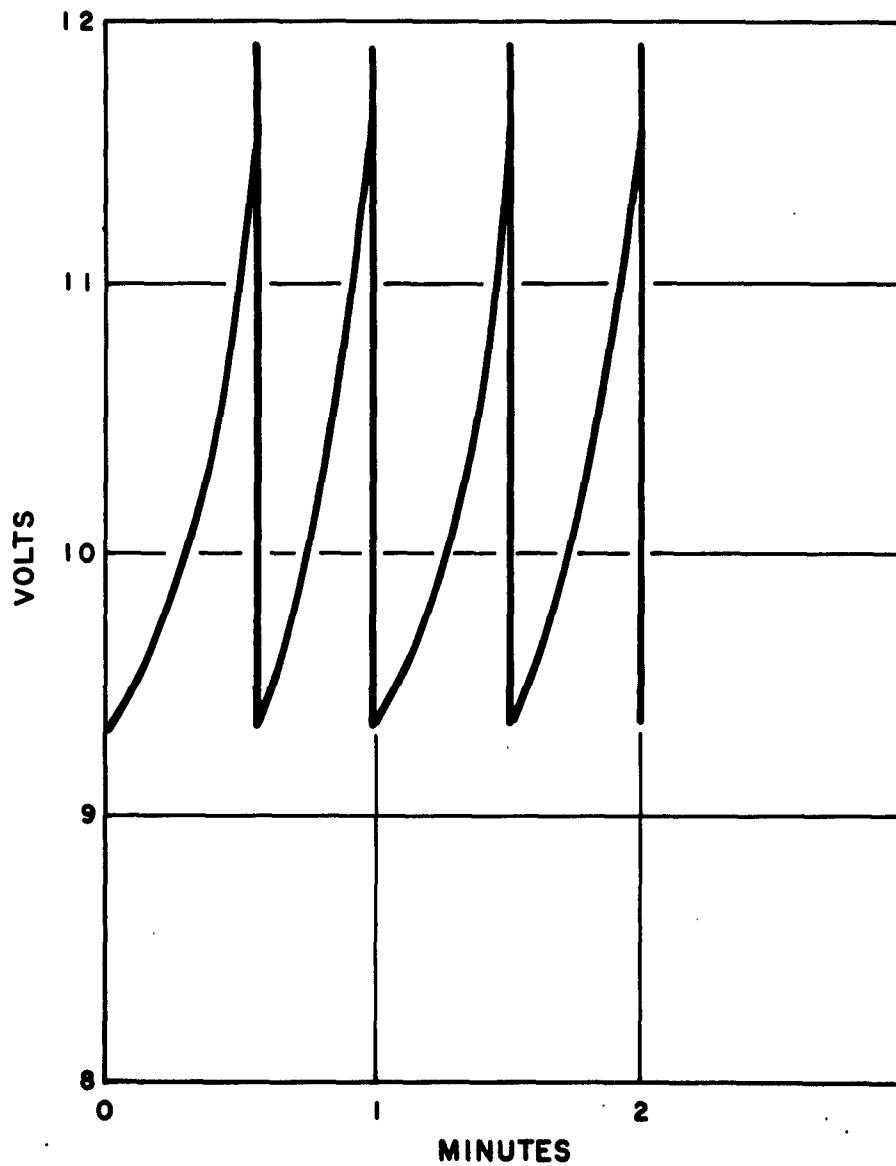## AT 0.6 HOURS

Figure 4c, Typical Run, Electrolytic Drying of HF
With Current Reversal

ELECTROLYSES IN ANHYDROUS HYDROGEN FLUORIDE

II.   The Hydrogen Fluoride – Nitrous Oxide System

by H. H. Rogers, S. Evans, and J. H. Johnson

The electrolysis of nitrous oxide solutions in anhydrous hydrogen fluoride has been shown to yield nitrogen trifluoride consistently, while oxygen difluoride and nitroxy fluoride were also produced frequently. Since nitrosyl fluoride may have been an intermediate, the electrolysis of the hydrogen fluoride-nitrosyl fluoride system was also investigated. The results are consistent with a mechanism requiring the formation of fluorine at the anode and nitric oxide at the cathode.

List of Figures

Introduction

The mechanism for the formation of products during electrolysis of nitrous oxide in anhydrous fluoride is not completely understood. The products can arise from the electrolysis of some electroactive species which forms on the addition of nitrous oxide to hydrogen fluoride or from the interaction of electrolytically generated fluorine with some species present in the system. The purpose of this paper is to elucidate the basic electrochemical mechanism in the hydrogen fluoride–nitrous oxide system through a study of polarization characteristics.

The electrochemical study was conducted in a Simons-type cell[1] with   (1)
the systems: hydrogen fluoride–sodium fluoride, hydrogen fluoride–sodium fluoride–nitrous oxide, and hydrogen fluoride–nitrosyl fluoride. Since nitrosyl fluoride was formed[2] on fluorination of nitrous oxide with   (2)
elementary fluorine at 100-900°,   it was deemed worthwhile to determine if nitrosyl fluoride was an intermediate in the electrochemical process. Nitrosyl fluoride reacts with the hydrogen fluoride electrolyte to form very stable complexes[3].   (3)

Polarization curves were determined in each of the above systems with the objective of seeking an inter-relationship between polarization phenomena and the products formed on electrolysis.

Experimental

Apparatus. The electrolytic cell and associated electrical equipment are fully described in the first paper[1] in this series. In addition, a stainless steel and Teflon vacuum line was used to collect and separate the products (Fig. 1). The system was also provided with storage cylinders and additional traps.

(Fig. 1)

Procedure. Referring to Fig. 1, hydrogen fluoride (Matheson Co., min. purity 99.9%) was added to the refrigerated cell as a liquid directly from the cylinder. Sodium fluoride (J. T. Baker Co., Reagent Grade), when used as a conductivity additive, was first dissolved in a small amount of hydrogen fluoride in a polyethylene bottle and then added to the electrolytic cell by means of a "T" in the inlet line. When completely anhydrous hydrogen fluoride was desired, the electrolyte was dried overnight by electrolysis using periodic current reversal[1].

Hydrogen Fluoride-Nitrous Oxide System. The nitrous oxide (Matheson Co. 98.0% min. purity) was added through an inlet valve in the cell cover; the gas was passed through the cell and condenser, and out the bypass valve to flush out all the helium, which had been used to prevent the entrance of moisture. After the bypass valve was closed, the cell pressure was permitted to rise to a maximum of 85 psig of nitrous oxide. This pressure was maintained for about one-half hour to ensure a saturated solution and then was reduced to atmospheric pressure by bleeding off the excess nitrous oxide. Any nitrous oxide remaining in the cell gas space was then purged with helium. The absorber (Fig. 1) removed

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any hydrogen fluoride which passed through the reflux condenser during electrolysis. A flow of about 30 cc/min of helium served to carry the products to the FEP Teflon traps which were cooled by liquid nitrogen. The products were separated from nitrous oxide by normal vacuum line techniques and were identified by their infrared spectra.

In this electrolysis, current was maintained constant at specific points over a range of 0.5 to 8.0 amps by a current regulator. The cell voltage was found to be between 5 to 8 volts depending upon the current settings, temperature, etc. Cell temperatures (internal) varied between -8 to -22°. The length of the runs varied from 1 to 3 hours. A porous Teflon divider (1/16-inch thickness, Porous Plastic Filter Co.) was used in about half the runs to separate the anode and cathode compartments in the liquid phase only.

Hydrogen Fluoride-Nitrosyl Fluoride System

Electrolyses in the hydrogen fluoride-nitrosyl fluoride system were carried out in substantially the same manner described above. Since the hydrogen fluoride-nitrosyl fluoride system is a good electrical conductor, a conductivity additive was neither needed nor used. The nitrosyl fluoride prepared by the method of Seel[3], was added as a solution in hydrogen fluoride. Additional details which differ significantly from those described under the hydrogen fluoride-nitrous oxide system are: cell voltage - 5 to 11 volts; cell temperature - -4 to -16° ; mole ratios, hydrogen fluoride to nitrosyl fluoride - 16:1 to 35:1. The porous Teflon divider was used in all experiments in this system.

The System, Hydrogen Fluoride-Nitrous Oxide

The solubility of nitrous oxide in hydrogen fluoride was determined as a part of this study. A plot of the vapor pressure measurements (Fig. 2) shows that the solubility is adequate for synthetic purposes, $\quad$ (Fig. 2) although it is apparent that the products of the electrolysis would be contaminated with nitrous oxide. Henry's law constants, calculated from the experimental data, are 7×10^{-6} at $-23°$ and 5×10^{-5} at $-78°$. The isotherms appear to follow Henry's law throughout the range considered, indicating a lack of reaction between solute and solvent. This point was partially confirmed by rough electrical conductivity measurements which showed that an insignificant increase in conductivity occurs with the addition of nitrous oxide to hydrogen fluoride. Therefore, a conductivity additive (sodium or potassium fluoride) was used for all electrolyses in the hydrogen fluoride-nitrous oxide system.

Electrochemistry of the Hydrogen Fluoride-Nitrous Oxide System

Electrolysis of the hydrogen fluoride-nitrous oxide system yielded nitrogen trifluoride consistently. In addition, either oxygen difluoride or nitroxy fluoride or both were generally formed. It appeared that the rate of formation of these latter products was greatest during the initial portion of the experiment. Varying the current during electrolysis did not appear to be significant in determining the nature of the products. Yields, based on current, of a typical experiment were: nitrogen trifluoride-2%, oxygen difluoride-2%, and nitroxy fluoride (NO_3F)-1%. The anodic weight losses during the electrolyses generally accounted for

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50 to 80% of the current. Since the hydrogen fluoride had been thoroughly dried in two of the experiments in which oxygen-containing products appeared, it is apparent that they originated with the nitrous oxide.

Anodic and cathodic polarization curves were determined with respect to a platinum reference electrode[2] in the hydrogen fluoride-potassium fluoride and hydrogen fluoride-sodium fluoride systems before and after the addition of nitrous oxide, as well as after the electrolysis was concluded. These curves were reproducible in general form but varied widely from run to run with respect to potential regimes. Since the applied potential for a given current density was highly reproducible in all experiments, it was concluded that the platinum electrode did not function effectively as a poised-type reference electrode in the hydrogen fluoride-sodium fluoride system. It did, however, clearly define at which electrode the phenomena occurred.

The applied polarization curves were generally reproducible, and it was reasonable to concentrate on the lower portion of the curve to highlight the basic processes which occurred in this system. Linear plots of current density versus applied potential in the low current density regions (i.e., up to 2 ma/sq cm which corresponds to a current of 0.16 ampere) yielded a consistent value for the decomposition voltage of dry hydrogen fluoride at nickel electrodes, namely, 3.9 volts (Fig. 4). (Fig. 4) A minimum current of 0.05 ma/sq cm was chosen arbitrarily as that corresponding to decomposition. These results were derived from several experiments in both the hydrogen fluoride-sodium fluoride and hydrogen fluoride-potassium fluoride systems. The shape and potential characteristics of the applied polarization curves obtained after the nitrous

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oxide was added and, after the electrolysis experiment was concluded, were virtually indistinguishable from those obtained in the pure system above.

Electrolyses in the Hydrogen Fluoride-Nitrosyl Fluoride System

Electrolyses in the hydrogen fluoride-nitrosyl fluoride system yielded only reduction products of the NO^+ ion with one exception; oxygen difluoride and nitroxy fluoride were products of one experiment where the hydrogen fluoride had been only partially dried. Not even traces of these compounds were found in those experiments where the hydrogen fluoride had been dried using periodic current reversal[1].

According to Seel[3], the electrolysis of hydrogen fluoride-nitrosyl fluoride solutions in a cell containing a diaphragm, which was capable of separating the gaseous products, should result in nitric oxide and fluorine as products.

In our cell, where no separation of the gaseous products was attained, the spontaneous reaction of nitric oxide and fluorine to give nitrosyl fluoride would be expected; the latter would, no doubt, dissolve in the electrolyte. The nitric oxide which was found as a product was probably a result of insufficient fluorine available from the anodic reaction. A substantial part of the current was used for the dissolution of the nickel anode.

The synthesis of nitrous oxide at the cathode is readily explained. It would be expected that the NO^+ ion would reduce directly to nitric oxide, although, with a sufficiently high cathode potential, reduction to nitrous oxide could also occur. The polarization curves (Fig. 3)   (Fig. 3)

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which were taken before the start of the run show clearly that a
second reaction took place at the cathode at currents over 1 ampere.

Discussion

Both the thermal fluorination[1] of nitrous oxide and the electrolysis of the hydrogen fluoride-nitrous oxide system resulted in the formation of nitrogen trifluoride. However, while nitrosyl fluoride was a product of the thermal reaction, oxygen difluoride and nitroxy fluoride were generally formed as a result of the electrolyses. The electrolyses of a hydrogen fluoride-nitrosyl fluoride solution produced neither oxygen difluoride nor nitroxy fluoride (with dry hydrogen fluoride). It is, therefore, probable that the formation of oxygen difluoride and nitroxy fluoride in the electrolysis of the hydrogen fluoride-nitrous oxide system was not the result of further electrolysis of any nitrosyl fluoride originally formed as an electrolysis product.

Representative polarization curves for the hydrogen fluoride-sodium (or potassium) fluoride system with and without added nitrous oxide are shown in Fig. 4. The residual current present before the solution was electrolytically dried was due to water and other impurities in the hydrogen fluoride which were removed by electrolytic drying. Such behavior is typical of systems with trace impurities. After drying, there was no residual current noted and the decomposition potential was found to be reproducible.

Since the addition of nitrous oxide does not affect the polarization characteristics of the cell, it is reasonable to conclude that there is a basic electrochemical reaction which is common to both systems, namely, the decomposition of hydrogen fluoride:

$$2HF \longrightarrow H_2 + F_2$$

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The anodic electrochemical reaction common to both systems appears
to be:

$$HF_2^- - e^- \longrightarrow HF + F\cdot$$

It is proposed that additional reactions were a result of the com-
bination of the electrolytically generated "active" fluorine with nitrous
oxide. Since the concentration of products which resulted from such a
postulated reaction was found to be low, most of the active fluorine
either formed fluorine or directly attacked the nickel anode. The cur-
rent equivalent of the weight loss during electrolysis of the hydrogen
fluoride-nitrous oxide system is not significantly different from that
derived from electrolysis of hydrogen fluoride-sodium fluoride. The
bulk of the current utilized in the electrolysis in the hydrogen fluoride-
sodium fluoride system can be related directly to the weight loss at the
anode. While the anode dissolution process might not have been a direct
electrochemical reaction, it can be related to the amount of fluorine
generated, assuming that the nickel was directly attacked by the active
fluorine.

Acknowledgment

Footnotes

1. The first paper in this series describes the electrolytic drying of "anhydrous" hydrogen fluoride. H. H. Rogers, S. Evans and J. H. Johnson (submitted for publication).

2. F. D. Marsh, U. S. 3,3032,400 May 1, 1962.

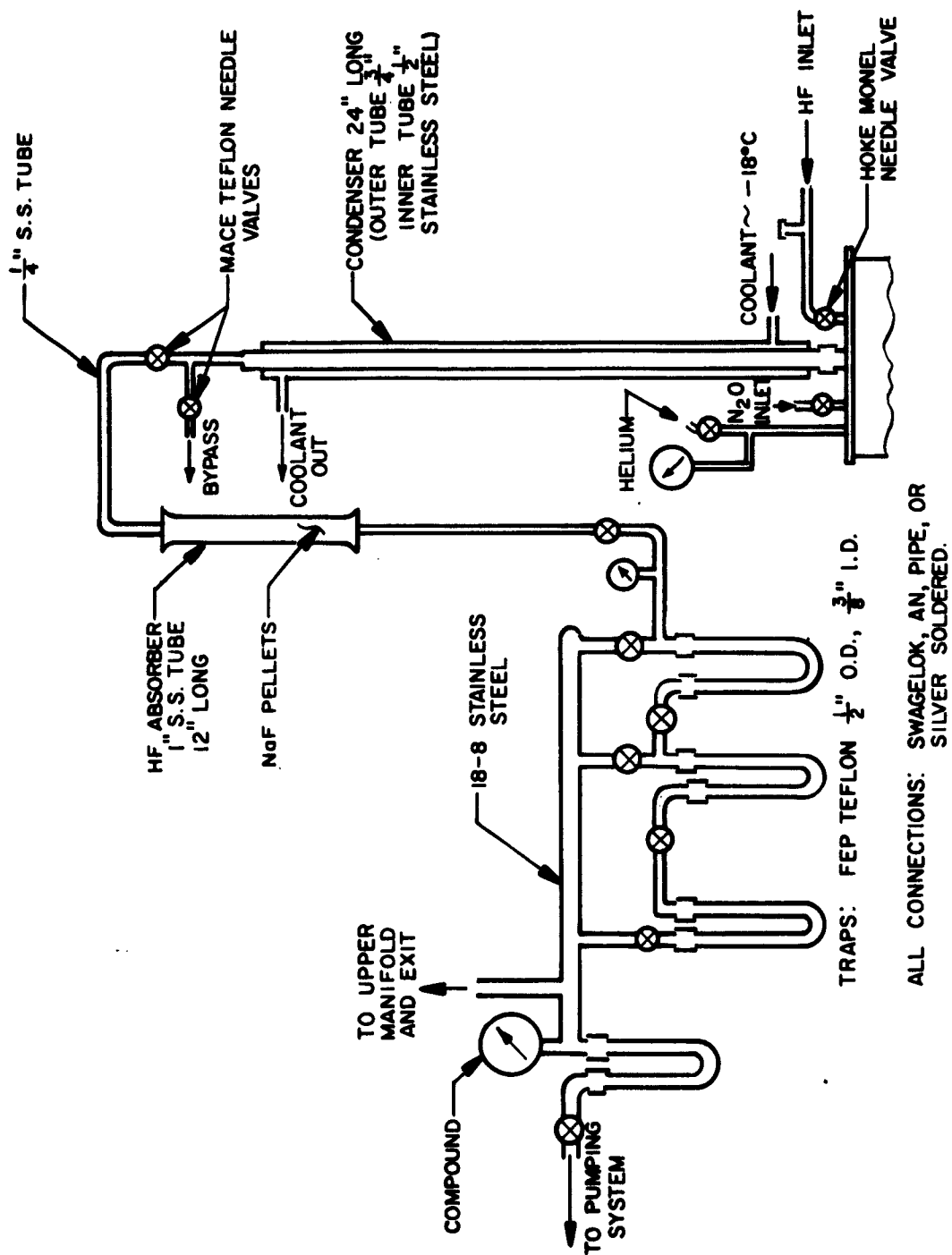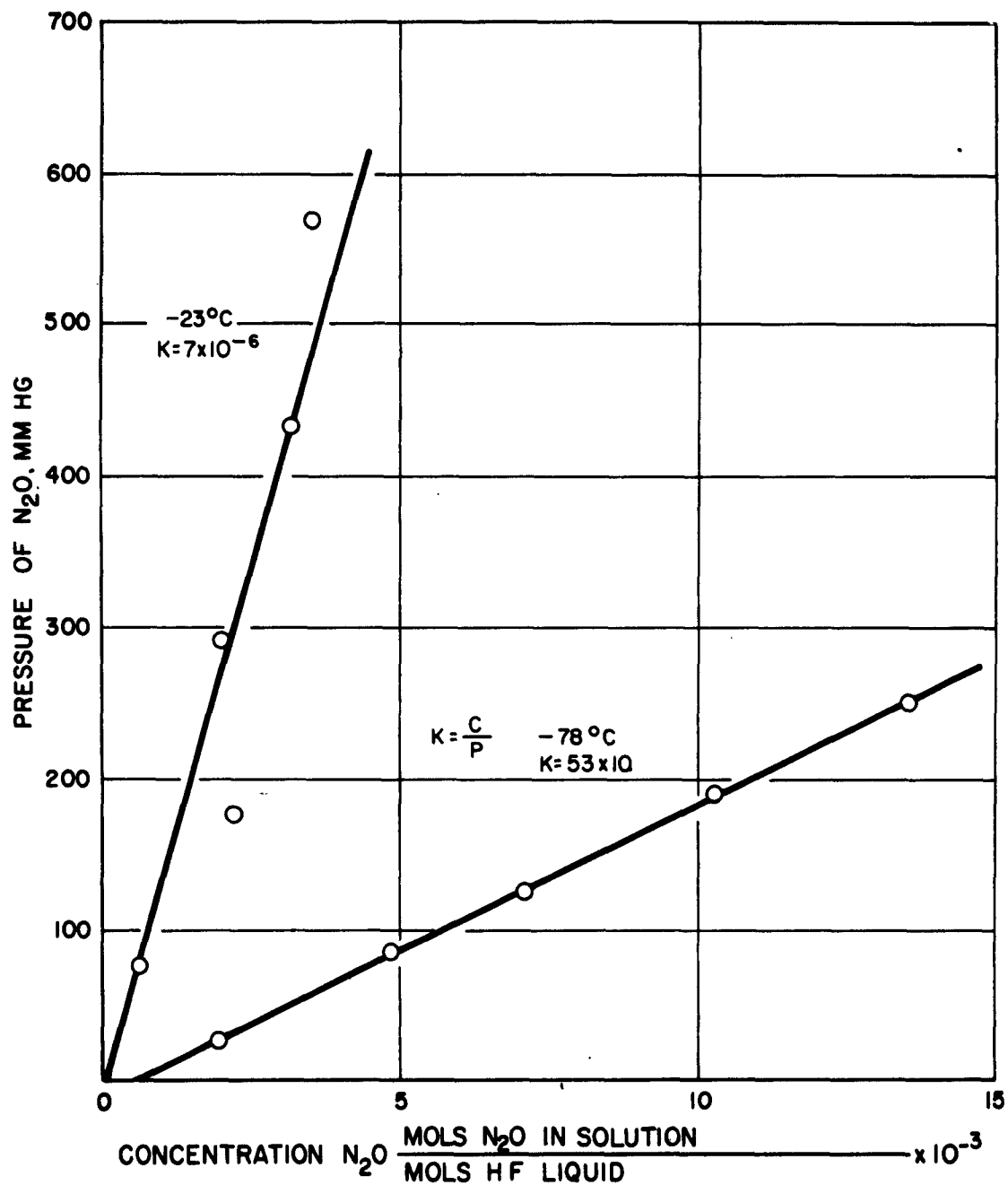3. F. W. Seel, W. Birnkraut and D. Werner Ber. 95, 1264-74 (1962).

¼" S.S. TUBE

MACE TEFLON NEEDLE VALVES

CONDENSER 24" LONG (OUTER TUBE ¾" INNER TUBE ½" STAINLESS STEEL)

HF INLET

HOKE MONEL NEEDLE VALVE

COOLANT ~ -18°C

BYPASS

COOLANT OUT

HELIUM

N₂O INLET

HF ABSORBER 1" S.S. TUBE 12" LONG

NaF PELLETS

18-8 STAINLESS STEEL

TO UPPER MANIFOLD AND EXIT

COMPOUND

TO PUMPING SYSTEM

TRAPS: FEP TEFLON ½" O.D., ⅜" I.D.

ALL CONNECTIONS: SWAGELOK, AN, PIPE, OR SILVER SOLDERED.

VALVES: HOKE MONEL, DIAPHRAGM OR BELLOWS TYPE.

Figure 1. Product Handling Equipment

Figure 2.   Solubility of $N_2O(g)$ in HF (ℓ), K in Mole Fraction/mm Hg
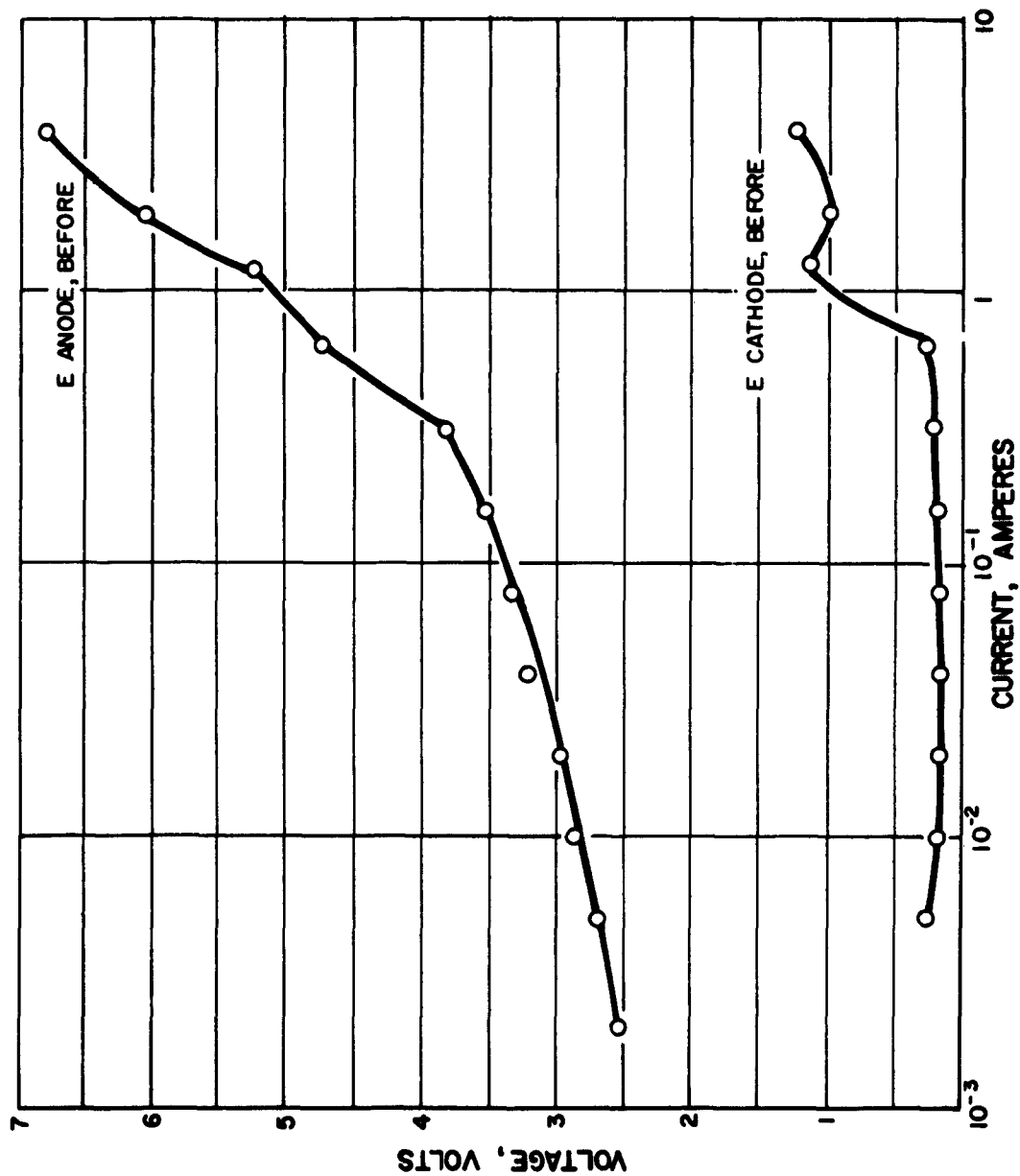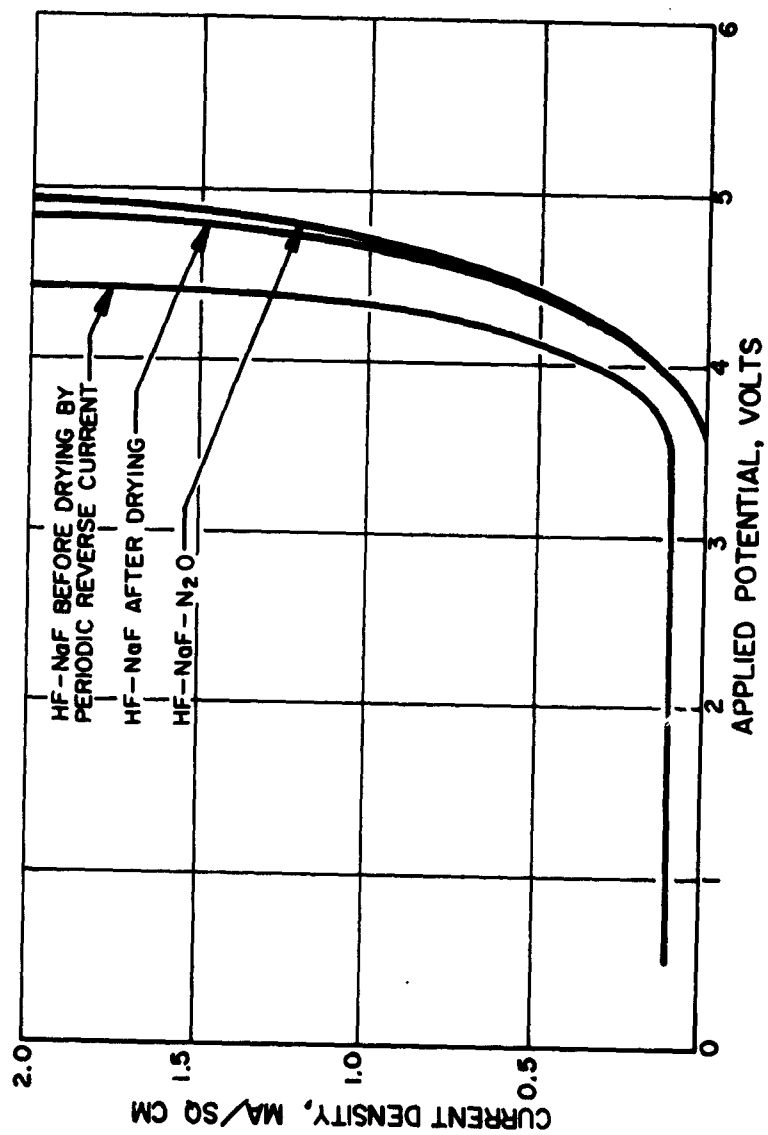
Figure 3. Polarization Curve 1F-F10

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Figure 4. Typical Behavior of Potential in Low Current Region

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ELECTROLYSES IN ANHYDROUS HYDROGEN FLUORIDE

III. The Hydrogen Fluoride-Dinitrogen Tetroxide System[1]   (1)

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The hydrogen fluoride-dinitrogen tetroxide system was studied in a
Simons-type cell using a three electrode system. Analysis of the anodic
polarization curves and the products formed at various applied currents
indicated the formation of a relatively noninsulating film at low cur-
rents. The apparent decomposition potential was identical for systems
of varying dinitrogen tetroxide concentration. In oxidizer-rich systems
(mole ratio $HF:N_2O_4$, 2:1 and 4:1) this potential corresponded to the
evolution of oxygen. In systems poorer in oxygen-containing species
(34:1 mole ratio) oxygen difluoride and oxygen appeared to be formed
simultaneously. In such systems, a limiting current region appeared
wherein the potential rose sharply and ozone was produced.

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Introduction

The electrochemical literature in anhydrous hydrogen fluoride deals mainly with conductance measurements[2], determination of equilibrium potentials used in the evaluation of free energies[3], and, more recently, in the development and use of dropping mercury electrodes[4]. Requisite factors in such studies are: solvent purity, electrode stability, nonpolarizable electrodes and operation at very low current densities.　　(2)　(3)　(4)

The electrochemical study described herein was conducted under conditions normally used in electrosynthesis. In a Simons·type cell with large electrodes where relatively large current densities are employed, and where no satisfactory reference electrode has been developed, it is not feasible to discuss results in terms of reversible electrode kinetics. Nevertheless, we have obtained useful electrochemical information which permitted a better understanding of phenomena occurring in these systems, afforded us the opportunity of testing some of the hypotheses which evolved from the analysis of such results, and proved useful in the elucidation of the most fruitful paths of study.

As a result of this and earlier investigations[1], a poised-type reference electrode was developed. This permitted the use of a three electrode system to separate anodic and cathodic effects while determining polarization curves, as well as during electrolysis. The purpose of this work was to gain further understanding of the electrochemistry in the hydrogen fluoride-dinitrogen tetroxide system by seeking an interrelationship between polarization phenomena and the products formed on electrolysis.

Experimental

The apparatus, reagents, and procedures used in this investigation were similar to those described in the earlier papers in this series[1]. Additional experimental details are described below.

The hydrogen fluoride-dinitrogen tetroxide solutions were prepared by slowly adding liquid dinitrogen tetroxide (Matheson Co., 99.5% min. purity) to hydrogen fluoride contained in the electrolytic cell. The hydrogen fluoride-nitric acid solutions were prepared by adding liquid hydrogen fluoride to finely powdered, dried lead nitrate (J. T. Baker, Co., Reagent Grade) under anhydrous conditions. The supernatant liquid was then added to the electrolytic cell. Analysis of the residue indicated almost complete conversion to lead fluoride.

It was discovered that a suitably constructed platinum electrode[1] maintained a steady potential in the hydrogen fluoride-dinitrogen tetroxide system in a high imedance measuring curcuit. Anodic and cathodic polarization curves were determined with respect to this electrode at specific current levels (maintained constant by a current regulator), starting at 0.025 ma/sq cm and increasing in steps up to 125 ma/sq cm. The polarization curves were generally determined before and after each electrolysis.

Cursory determination of the specific conductivity of the hydrogen fluoride-dinitrogen tetroxide solution (mole ratio, 31:1) revealed that it was of the same order of magnitude as that determined (in the same cell) for a saturated aqueous sodium chloride solution at $0°$ (10^{-1} ohm^{-1} cm^{-1}). The conductance values were determined at 1000 cycles in a Kel-F conductivity cell having bright platinum electrodes. In practice, the solution resistance between the anode and cathode was so

low, that even at high current densities, the contribution from IR drops
of solution could be neglected because they were less than the experimental
errors.

The electrodes were nickel and were prepared by mechanical treatment
(abrasive paper or wire brush) or by treatment with nitric acid. In some
cases, only a water rinse was used.

In all cases, the electrolyses were conducted at constant currents
over a range of current densities of 10 ma/sq cm to 125 ma/sq cm although
most experiments were carried out at 100 ma/sq cm. Cell temperatures
varied between -2 and -19°   depending on cell power dissipation, ambient
temperature, etc. Runs varied in length from 1/2 to 2-1/2 hours. Anal-
ysis of the products was made by infrared and by mass spectra.

Results

Typical anodic polarization curves expressed on a semilog scale in the 34:1 molar ratio system are characterized into regions in the order of increasing current density as follows (Fig. 1):

A - Extremely low current densities where it is difficult to obtain data. Points in this region are highly irreproducible.

B - Reproducible linear region having β values (slopes) between 0.3 and 0.38.

C - Limiting current region, i.e., limiting current varied between 15 and 50 ma/sq cm.

D - Time dependent region, i.e., extensive depolarization occurred with passage of current.

Before determining the products formed in each region, it was necessary to characterize the behavior of the nickel anode in anhydrous hydrogen fluoride. It was found that open circuit corrosion rates were so low that long exposure times were required to obtain significant weight losses. Nickel electrodes were exposed to various hydrogen fluoride systems overnight. The resulting weight losses were converted into corrosion currents in accordance with Faraday's Law (Table I). In addition, typical weight losses during electrolysis were converted into equivalent currents of dissolution (Table I). No visible attack was observed on electrodes used in the electrolysis of hydrogen fluoride-dinitrogen tetroxide mixtures for periods as long as 2 hours. Nickel dissolution is of minor significance in the interpretation of the polarization curve (Fig. 1) and is probably restricted to region A.

TABLE I

DISSOLUTION RATES OF NICKEL IN

HYDROGEN FLUORIDE SYSTEMS

System	Electrolysis Current, ma/sq cm	Open Circuit Corrosion Rate, ma/sq cm	Current Equivalent of Dissolution, ma/sq cm
HF	---	0.0017	---
HF-NaF	---	0.0088	---
HF-N_2O_4	---	0.0023	---
HF	25	---	4.4
HF-NaF	38	---	8.8
HF-N_2O_4	10	---	0.16
HF-N_2O_4	100	---	0.16

Region B (Fig. 1) was reproduced in polarization curves determined
before and after electrolysis was carried out. The magnitude of the
limiting current (region C) did not vary in a definite manner in curves
determined before and after electrolysis except when the nickel had been
pretreated with nitric acid. In such cases the magnitude of the limiting
current was of the same order before and after electrolysis.

Representative linear plots of anodic polarization curves determined
in hydrogen fluoride–dinitrogen tetroxide systems (mole ratio 34:1 and
2:1) and in hydrogen fluoride–nitric acid (mole ratio 17:1) are shown in
Fig. 2. It is noteworthy that the apparent decomposition potentials of   (Fig. 2)
these systems coincide. This suggests that an initial electrochemical
process is common to all three systems. The products of electrolysis in
these systems at various current densities are listed in Table II. Oxy-
gen was the only product detected in the electrolysis of the 2:1 ratio
system. This was true whether or not the divided cell was used, the
hydrofluoric acid was electrolytically predried[4], or a small percent of
water was intentionally added. The slope (β) of the linear portion of
the semilog plot for this system was 0.2.

In the hydrogen fluoride–dinitrogen tetroxide system (mole ratio
34:1) electrolysis in region B yielded oxygen and oxygen difluoride as
products which were independent of electrode preparation (divided or
undivided cell), and predrying of solutions. Based on sampling of pro-
ducts during electrolysis at 10 ma/sq cm, it was estimated that a minimum
of 0.25 ma/sq cm was utilized in the formation of oxygen while an approx-
imately equal amount of current was used for the production of oxygen
difluoride.

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TABLE II

PRODUCTS FORMED DURING ELECTROLYSIS IN HYDROGEN FLUORIDE

System	Mole Ratio, HF:Oxidizer	Current Density Electrolysis, ma	Products
$HF-N_2O_4$	2:1	300	O_2
$HF-N_2O_4$	2:1	100	O_2
$HF-N_2O_4$	4:1	100	O_2
$HF-N_2O_4$	34:1	10	O_2, OF_2
$HF-N_2O_4$	34:1	100	O_2, OF_2, O_3
$HF-HNO_3$	17:1	100	O_2, OF_2, O_3

Operation at currents above the limiting current consistently yielded oxygen, oxygen difluoride, and ozone. The amount of oxygen difluoride corresponded to only a few percent of the total current passed. It was estimated that ozone production corresponded to about 10 percent of the current passed

At electrolysis above the limiting current density in the 34:1 system (region D), the anode potential decreased within about 15 minutes to a reproducible value at which it remained for periods as long as 2 hours (Fig. 3). The cathode potential remained constant with time while the (Fig. 3) applied potential varied in the same manner as the anode potential. This confirms the opinion that the depolarization resulted from a process occurring at the anode. At these high current densities the temperature of the cell rose a few degrees. However, identical behavior (Fig. 3) was noted in experiments conducted at $0°$, indicating that the depolarization was not a temperature effect. Interruption of the current for a few minutes once the steady potential had been obtained, followed by resumption of electrolysis at the same current density, resulted in depolarization identical to that illustrated in Fig. 3. This behavior was independent of the use of a diaphragm, electrolytic drying, and electrode preparation. This behavior was not observed in similar experiments in the hydrogen fluoride-nitric acid system where the same products were obtained.

Once the steady potential was achieved, anodic polarization curves were determined by gradually lowering the current, without current interruption, and measuring the resulting anode potentials (determining the curve backwards). Representative behavior is illustrated in Fig. 4. (Fig. 4) The dashed curve represents the anodic polarization curve determined in

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the usual manner. Region B was reproduced (β value was the same) in determining the curve backwards[1]. Erratic behavior was noted in initially determining the curve backwards whenever the current was momentarily interrupted.

Cathodic polarization curves were determined in each experiment, and cathode potentials were periodically monitored during electrolysis. Since the reference electrode was in close proximity to the anode, the cathode potentials included contributions of IR drops as well as factors which might arise from geometrical considerations. Generally the cathode potential was a small portion of the total applied potential. The open circuit potential of nickel in the 34:1 system was of the order of 0.4 volts, anodic to the platinum reference electrode. The cathodic polarization curve exhibited little polarization from this value as a function of applied current. It was noted however, that once cathodic potentials greater than 1 volt were achieved, nitrous oxide was produced. Such potentials were found in the hydrogen fluoride-dinitrogen tetroxide system after prolonged electrolysis at 100 ma/sq cm or after deliberately subjecting the cathode to anodic pretreatment in hydrogen fluoride prior to the addition of dinitrogen tetroxide. In the hydrogen fluoride-nitric acid system, cathodic potentials greater than 1 volt were attained at current densities greater than about 10 ma/sq cm. The cathode potential during electrolysis at 100 ma/sq cm in this system was of the order of 2 volts. Nitrous oxide was a consistent product, although in minor concentration.

Discussion

The open circuit corrosion rate of nickel in anhydrous hydrogen fluoride is extremely small and is not markedly affected by additions of sodium fluoride or dinitrogen tetroxide (Table I). Such additions increase the solution conductivity by a factor of at least 1000 and also markedly increase the fluoride ion concentration. Based on the evidence that the corrosion rate is not affected by increased solution conductivity, increase in fluoride ion concentration, or the presence of an efficient cathodic depolarizer (dinitrogen tetroxide), it is reasonable to conclude that the corrosion process is under anodic control. Interpreted in terms of local cell theory[5], nickel dissolution at anodic areas probably results (5) in a tightly adherent insoluble film of nickel fluoride which then becomes a more noble or cathodic site. Thus the low corrosion rate is explained by the diminishing number of electrochemical cells caused by the stifling of anodic sites.

The anodic dissolution processes are quite different when current is passed between the electrodes. Thus nickel dissolution during electrolysis proceeded at a rate 25 to 50 times greater in the hydrogen fluoride or hydrogen fluoride-sodium fluoride systems than in the hydrogen fluoride-dinitrogen tetroxide system. It is proposed that a film was formed on nickel in the hydrogen fluoride-dinitrogen tetroxide system as a result of the application of very low currents (region A) which rendered it passive. This is reasonable, in light of the known tendency of nickel, to passivate in oxidizing media. The many studies of passivity of nickel and iron in aqueous oxidizing media show that, once passivity is accomplished, the anode potential rises until another electrochemical reaction

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takes place. Invariably this reaction is the evolution of oxygen[6]. If,   (6)
as a result of this new process, the current then increases, the phenom-
enon is called transpassivity; region B is the region of transpassivity
in the systems presented here. Thus, for all intents and purposes the
electrolyses in hydrogen fluoride-dinitrogen tetroxide systems represent
reactions carried out at a passive nickel electrode where the initial
reaction is the evolution of oxygen. In effect, as a result of passivity,
nickel behaves as a noble unattackable electrode. The fact that the
apparent decomposition potentials (Fig. 2) of the various systems coin-
cide, suggests a common reaction. In the system rich in oxygen-containing
species (2:1 ratio), oxygen was the only anodic product. It is concluded,
therefore, that the limiting current was a function of the oxygen-
containing species. At currents in region B, lower concentrations of
dinitrogen tetroxide limited the extent to which oxygen could be pro-
duced and as a result oxygen difluoride formed. In such systems further
increase in current resulted in severe polarization and ozone was formed.

Little is known of the electroactive species present in the hydrogen
fluoride-dinitrogen tetroxide system. A solution of dinitrogen tetroxide
in hydrogen fluoride has been separated by distillation into a solution
of nitric acid in hydrogen fluoride and a solution of nitrosyl fluoride
in hydrogen fluoride[7]. It is likely, therefore, that the reaction of   (7)
hydrogen fluoride and dinitrogen tetroxide can be represented by:

$$2HF + N_2O_4 \rightleftharpoons NO^+ + HF_2^- + HNO_3$$

$$2HF + HNO_3 \rightleftharpoons H_2NO_3^+ + HF_2^- .$$
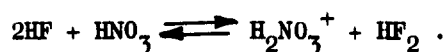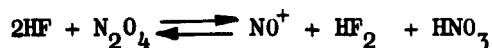
The oxygen-containing products formed on electrolysis did not result from water present in the hydrogen fluoride since the system was electrolytically dried. This does not preclude the possibility that water was formed as a cathodic product as a result of a highly depolarized electrode reaction such as

$$H_2NO_3^+ + e^- \longrightarrow NO_2 + H_2O$$

In addition, it has been proposed[8] that water is formed as a result of the reaction

$$H_2NO_3^+ + 2HF \longrightarrow NO_2^+ + H_3O^+ + HF_2 \; .$$
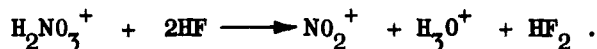
The possibility, then, that the products obtained are a result of the electrolysis of water cannot be excluded, and merit further study. With this in mind, the systems rich in dinitrogen tetroxide (2:1 and 4:1) would contain more water than the 34:1 mole ratio system. In the latter system concentration of water would limit the potential achieved for a given current density.

It would be unreasonable to expect reproducibility in the magnitude of the limiting current under the conditions of our experiments. Strict interpretations of the magnitudes of such currents are restricted to basic studies using nonpolarizable electrodes (platinum or dropping mercury), and under conditions where it is possible to determine limiting rates as a function of area, stirring rate and concentration of various species. On the basis of the evidence here, it is not possible to state whether the rate limiting region C was a result of transport of some species to the anode, desorption of some species, electrolysis of an adsorbed species, or a type of gas-film polarization.

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Stern points out that β values have meaning for uncomplicated reactions but are often difficult to interpret when consecutive reactions are occurring[9]. The fact, however, that these values are reproducible (9) in the 34:1 ratio system regardless of how the curve was determined, indicates that the same reactions are occurring each time. The value for the 2:1 system probably represents that for the evolution of oxygen.

The depolarization caused by electrolysis at high current densities is not fully understood. The polarization curve, which was determined backwards, suggests that some unstable electroactive species is produced at the anode, which in effect autocatalyzes the anodic reaction. The fact that momentary current interruption destroys this "depolarization" and that use of the divider does not affect it supports this view.

The nickel anodes did not appear significantly different after electrolysis in the hydrogen fluoride-dinitrogen tetroxide systems or in the hydrogen fluoride-nitric acid system. According to the "oxide-film" theory of passivity[10] an adherent and invisible film of oxide forms on (10) the anode which separates the metal from its environment; when coverage is complete oxygen evolution commences. The "adsorption theory" of passivity[11] favors the formation of a chemisorbed film of oxygen or pas- (11) sive ions. The presence of uncoupled electrons in the d orbitals of nickel would account for the strong bond formation with some component of the environment, particularly a species which also contains uncoupled electrons (e.g., oxygen) thus resulting in electron pair or covalent bonding supplementary to ionic bonding.

It is unlikely that an oxide film would be stable in hydrogen fluoride media. However, this does not preclude the possibility that an

oxide film was maintained during the passage of current. When the current was interrupted the potential of the nickel electrode returned to its original value after several minutes.

Other experiments revealed that noble metals such as platinum and palladium underwent severe attack before useful anodic potentials could be attained. In contrast, a highly insulating film formed on monel so that abnormally high applied potentials were required to conduct electrolyses. Electrolysis with a monel anode resulted in the same products as those obtained with a nickel anode. This evidence supports the view that the apparent nobility of nickel was caused by the formation of a relatively noninsulating passive film.

Acknowledgement

References

1. Earlier papers in this system have concerned: (a) The electrolytic drying of hydrogen fluoride, H. H. Rogers, S. Evans and J. H. Johnson (submitted for publication) (b) The hydrogen fluoride-nitrous oxide system, H. H. Rogers, S. Evans and J. H. Johnson (submitted for publication).

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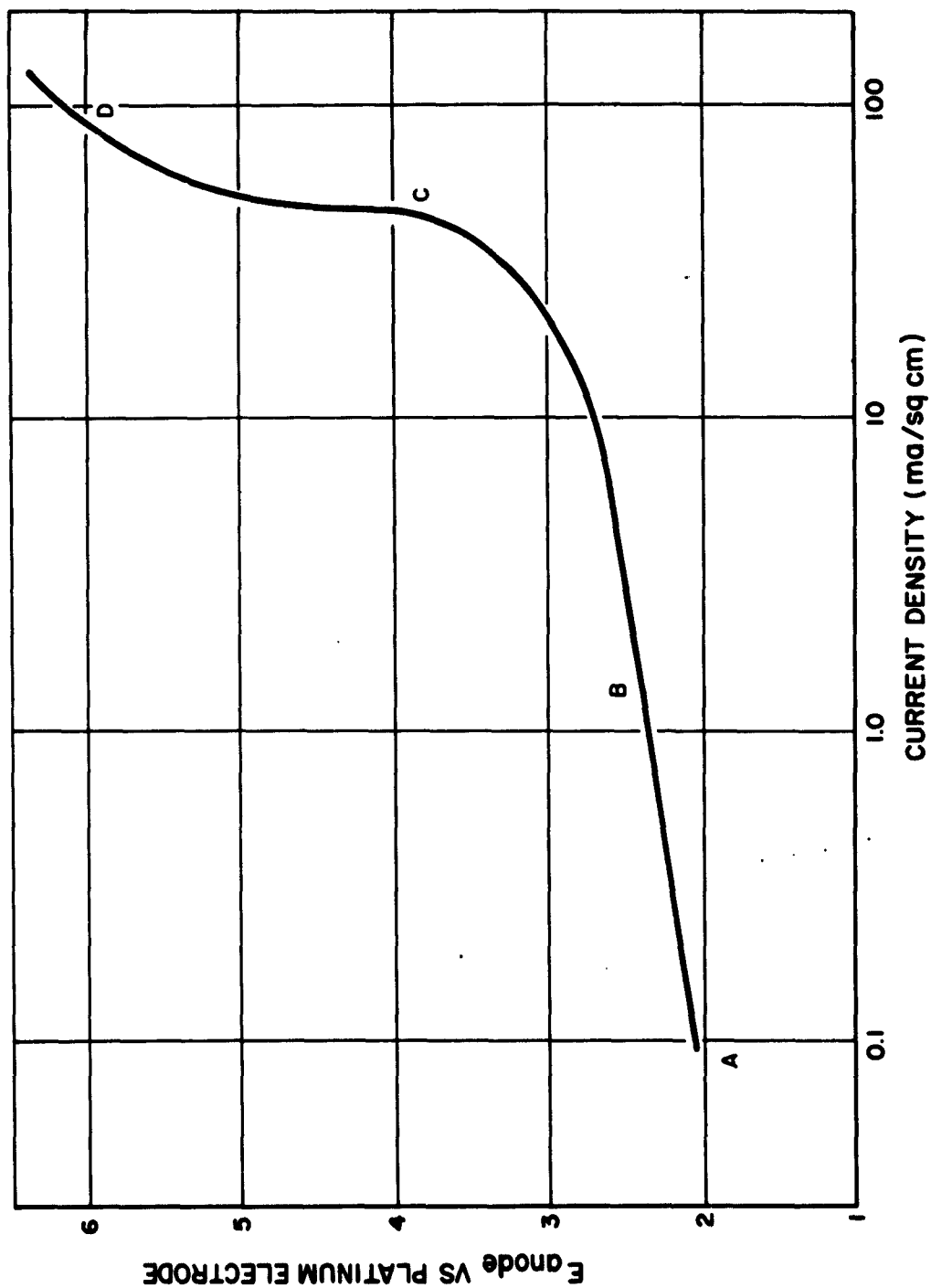11. H. H. Uhlig and P. F. King; J. Electrochem. Soc., 106, 1-6, (1959).

Figure 1. Typical Anodic Polarization Curves Determined on Nickel in the $HF:N_2O_4$ (mole ratio 34:1) System
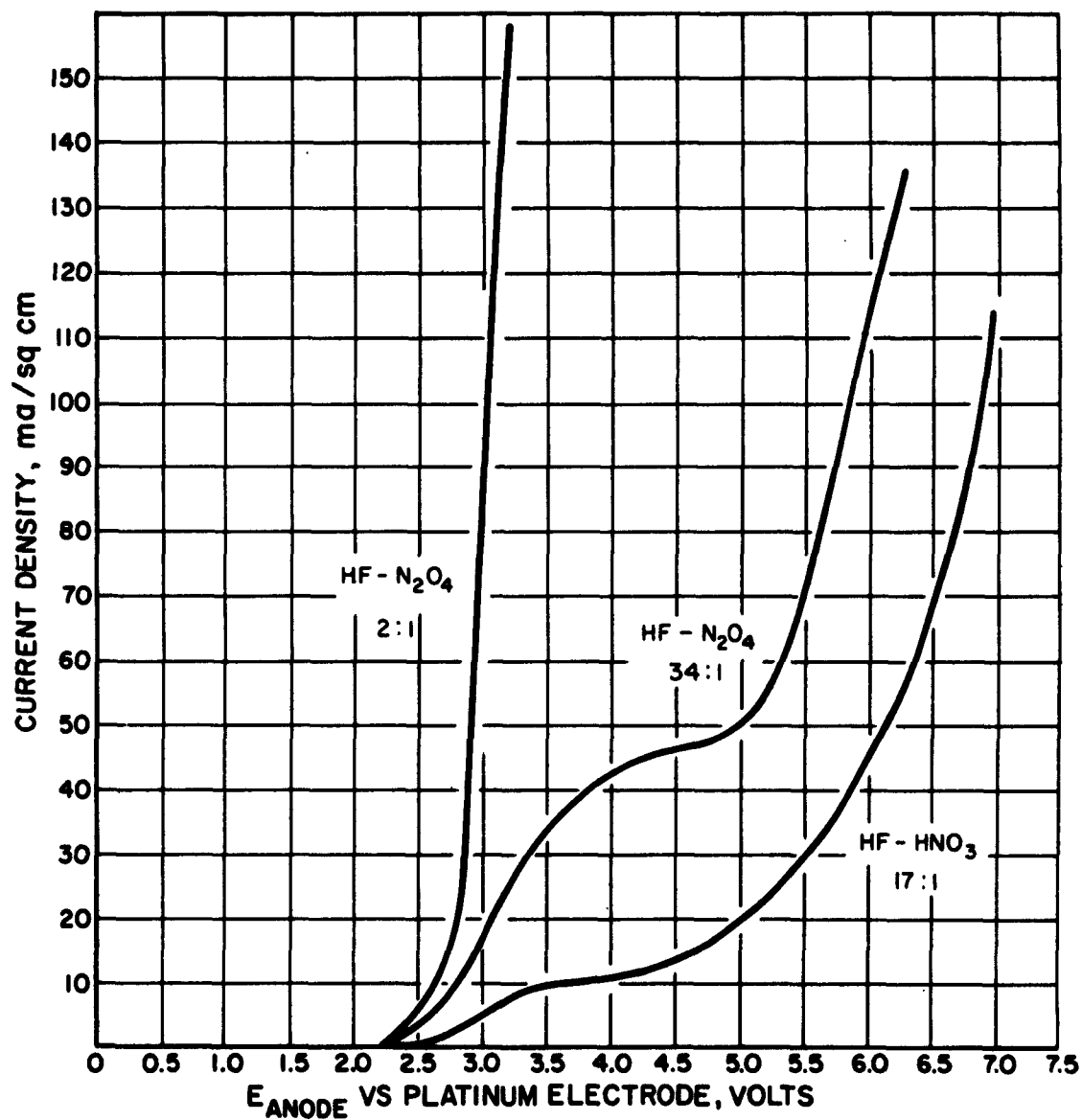
17

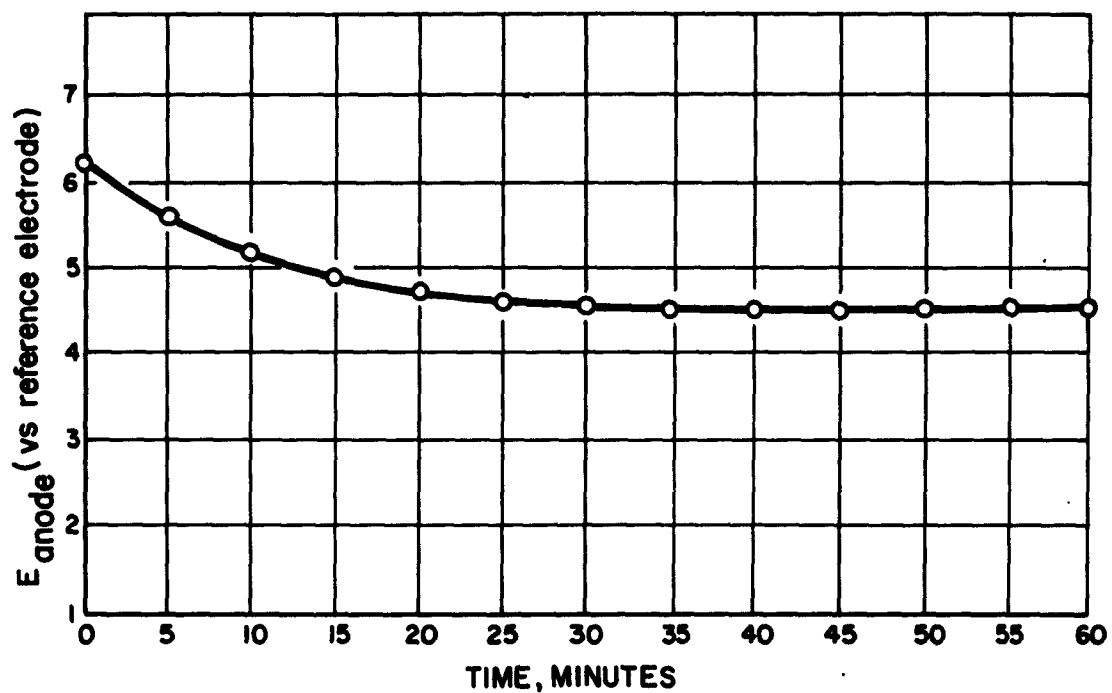Figure 2. Typical Anodic Polarization Curves Determined on Nickel

Figure 3. Typical Plot of Anodic Potential as a
Function of Time of Electrolysis (current
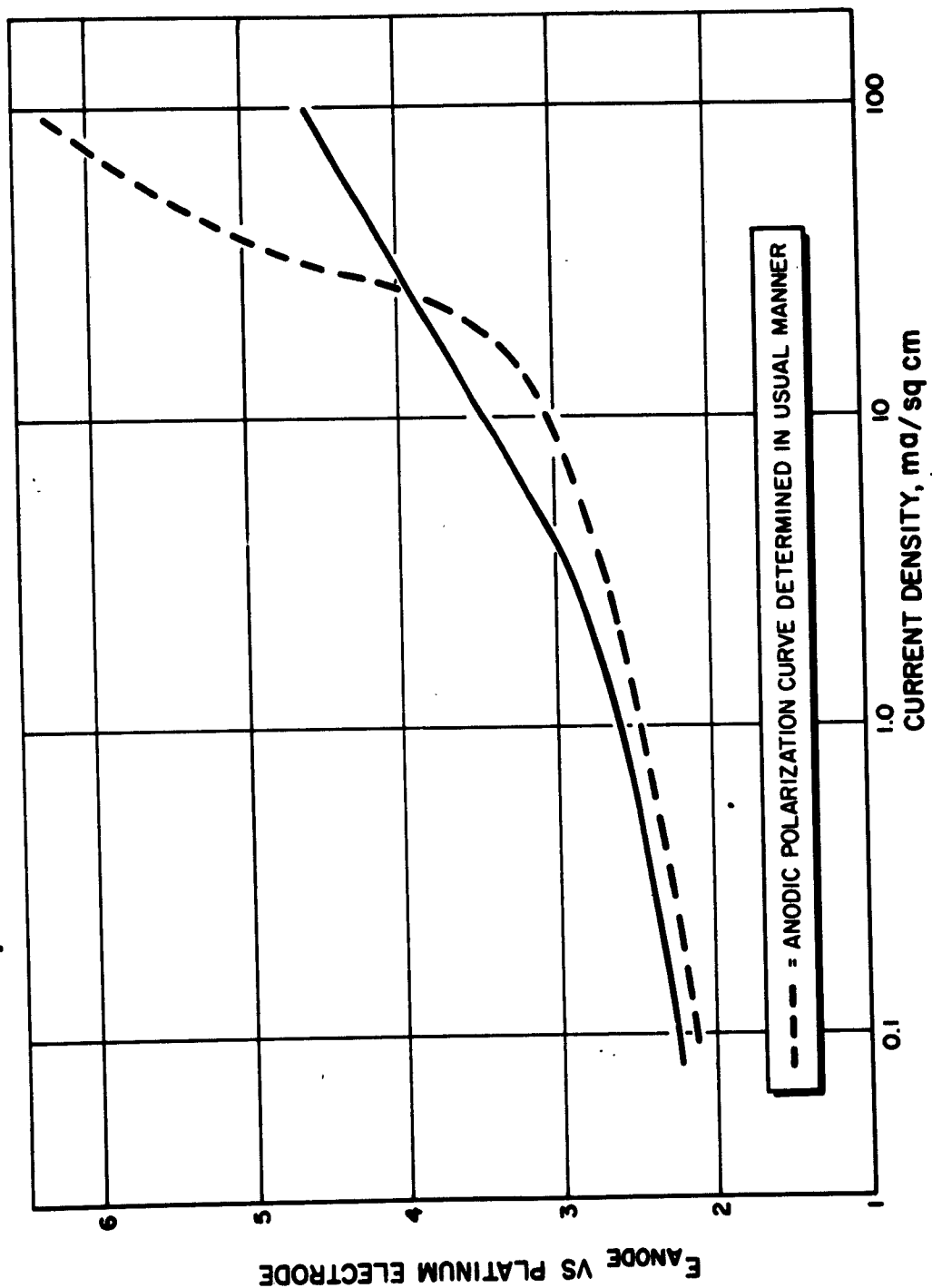density - 100 ma/sq cm., current - 8
amperes)

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Figure 4. Anodic Polarization Curve on Nickel in HF-N$_2$O$_4$ (mole ratio 34:1) System, Obtained by Successively Lowering the Current After Prepolarizing to a Steady Anode Potential at 100 ma/sq cm.

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ELECTROLYSES IN ANHYDROUS HYDROGEN FLUORIDE

IV. The Hydrogen Fluoride-Nitric Oxide System

by S. Evans, H. H. Rogers and J. H. Johnson

The hydrogen fluoride-nitric oxide system was studied using a three electrode system. Experimental evidence indicated that the anodic polarization curve on nickel was a form of passivity curve. Electrolysis above the limiting current for passivity resulted in no anodic attack and in the formation of oxygen difluoride. Electrolysis below this current level resulted in severe metal attack and in the formation of nitroxy fluoride. Electrochemical techniques are described which successfully delayed the onset of passivity so that subsequent electrolysis above the limiting current density resulted in the formation of nitroxy fluoride.

List of Figures

Introduction

Previous investigations[1] have shown that nickel behaved as an   (1)
unattackable, noble anode during electrolysis in the hydrogen fluoride-
dinitrogen tetroxide system. Oxygen, oxygen difluoride, and ozone were
produced at successively higher anodic potentials. Since a passive
film did not form during the electrolysis of anhydrous hydrogen fluoride
and anhydrous hydrogen fluoride-sodium fluoride systems, it was concluded
that film formation was related to the presence of dinitrogen tetroxide.
In aqueous media, passive film formation on metals such as iron and
nickel have been related to the strength of the oxidizing agent[2]. It   (2)
was decided to determine whether the addition of a weaker oxidizing agent
(i.e., nitric oxide) to hydrogen fluoride would delay the onset of
passivity in such a manner that the anodic products which occur at
passivated and nonpassivated nickel could be distinguished.

Cursory experiments revealed that the products of electrolysis in
the hydrogen fluoride-nitric oxide system varied from experiment to
experiment both in nature and in magnitude. Nitroxy fluoride and/or
oxygen difluoride was produced. The purpose of this paper is to discuss
the electrochemical behavior of nickel in the hydrogen fluoride-nitric
oxide system and relate such behavior to the products formed on
electrolysis.

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Experimental

The apparatus, reagents, and techniques used in this work are similar to those described previously[1,3,4]. The experiments were carried out in the same "Simons" type cell. Polarization curves were determined using a three electrode system in which platinum served as a reference electrode. (3-4)

The nitric oxide (Matheson Co., 99.0% min. purity) was added to the cell using the procedure employed earlier with nitrous oxide[3]. As in the case of nitrous oxide, the mole ratio of hydrogen fluoride to nitric oxide was a function of gas solubility. Electrolyte solutions obtained with this procedure were essentially saturated and no attempt was made to use lower nitric oxide concentrations.

Nickel electrodes were prepared by mechanical treatment (abrasive paper or wire brush); no acid treatment was employed in this work.

The electrolyses were carried out under constant current conditions, over a range of current densities of 15 ma/sq cm to 50 ma/sq cm. Cell temperatures were found to vary from 0 to -16°.

Results

Typical anodic polarization curves which were determined on nickel in the hydrogen fluoride-nitric oxide system can be divided into two regions (Fig. 1), each characterized by a different rate of polariza-   (Fig. 1) tion. Experiments were designed to establish the reactions which predominated during electrolysis in each region. Before proceeding to such experiments it was necessary to evaluate contributions due to the solution resistance and the corrosion of the nickel electrode.

A limited study of the solubility of nitric oxide in hydrogen fluoride at about -23° indicated that the Henry's law constant was 10^{-5} moles/moles-mm. That is, the solubility was close to that found for nitrous oxide[3]. However, unlike the nitrous oxide system, the hydrogen fluoride-nitric oxide system was a good conductor of current. The contribution due to solution resistance in the hydrogen fluoride-nitric oxide system was neglected, since in region A (Fig. 1) it was too low to be significant, while in region B it was within the experimental error. The open circuit corrosion rate of nickel in this system was of the order of 0.004 ma/sq cm, a value not significantly different from that obtained in hydrogen fluoride alone, or in hydrogen fluoride-dinitrogen tetroxide solutions. The open circuit corrosion current is far below any point on the anodic polarization curve (Fig. 1).

The major anodic product which resulted from electrolyses conducted at currents in region B was oxygen difluoride; trace quantities of nitroxy fluoride were occasionally detected. Close scrutiny of electrolysis experiments conducted at 40 ma/sq cm (region B) revealed that nitroxy fluoride was formed only during the first 10 minutes of the

experiment. Examination of Fig. 2, a plot of the anode potential vs   (Fig. 2)
time of electrolysis at 40 ma/sq cm, indicated that nitroxy fluoride
was formed only at lower potentials, while at higher potentials oxygen
difluoride was produced. It was hypothesized that nickel was passivated
as a result of electrolyses in region B, and that during the time
required to achieve complete passivity, nitroxy fluoride was formed.
There was no evidence of anodic attack during these electrolysis experi-
ments. It was then postulated that delaying the onset of passivity
would favor the formation of nitroxy fluoride.

Anodes were pretreated by electrolysis in region A. The anodic
potentials which resulted from electrolysis at 15 ma/sq cm are shown in
Fig. 3A. No gaseous products were found as a result of this electrol-   (Fig. 3A)
ysis. The current density was raised to 25 ma/sq cm (Fig. 3B) and then (Fig. 3B)
to 48 ma/sq cm (Fig. 3C). Electrolysis in these regions yielded only   (Fig. 3C)
nitroxy fluoride. After the experiment there was a significant amount
of material in the bottom of the cell which was subsequently found to
be nickel fluoride. The anode was characterized by the appearance of a
greenish yellow, flaky, nonadherent deposit of nickel fluoride. An
electrolysis experiment conducted at 15 ma/sq cm for several hours
yielded nitroxy fluoride as the major product, although there was also
a minor yield of oxygen difluoride. The current equivalent of the weight
loss of nickel as a result of this electrolysis was 1.6 ma/sq cm.

An electrochemical exploration of the effect of activating the
anode by pretreatment in region A (Fig. 1) is illustrated in Fig. 4.   (Fig. 4)
The anode was pretreated by electrolysis at 6.3 ma/sq cm for 1 hour.
Subsequent increase of current to 40 ma/sq cm did not result in increased
polarization. The anode potentials were considerably lower than those

which resulted from electrolysis experiments conducted exclusively at 40 ma/sq cm (Fig. 2). At 130 ma/sq cm the anode potential oscillated between 4 and 5.5 volts. It was suspected that this represented the metastable region commonly encountered in passivity curves[2]. The use of constant current techniques for determining polarization curves precludes direct investigation of the metastable region. Subsequent increase of the current to 163 ma/sq cm resulted in complete passivity. Thus, the potential remained at a high value when the current was then lowered to 56 ma/sq cm and held at that value for 20 minutes. Oxygen difluoride was formed in this latter region.

Earlier investigations[4] revealed that the use of current reversal techniques during the electrolysis of hydrogen fluoride was more effective than conventional methods (no reversal) in producing dry hydrogen fluoride. Current reversal resulted in marked anode depolarization which allowed higher currents to pass than were possible with no reversal. It was shown that this higher current was related to water removal. An experiment was conducted in the hydrogen fluoride-nitric oxide system using current reversal techniques. The ratio of reversals was arbitrarily chosen as 3:1. Thus the normal anode repeatedly acted as an actual anode for 30 seconds and as a cathode for 10 seconds. During electrolysis at a current density of 25 ma/sq cm for 2 hours the anode potential rose to 7.8 volts from an initial value of 6.7 volts. Nitroxy fluoride was the major anodic product which resulted. After subsequent addition of more nitric oxide the electrolysis was continued at 50 ma/sq cm for 10 minutes and then at 88 ma/sq cm for an additional 10 minutes. With normal techniques (no reversal) such currents required an abnormally high applied voltage and therefore could not be effectively achieved.

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The products which resulted at these higher currents were nitroxy fluoride and traces of oxygen difluoride. The current equivalent of nickel dissolution in this experiment conducted at three different currents was 0.75 ma/sq cm for the anode while it was acting as the anode and 0.69 ma/sq cm for the cathode during the time it was the anode.

An experiment was also carried out in the hydrogen fluoride-sodium fluoride oxide system during electrolysis (no current reversal) at 6.3 ma/sq cm, 25 ma/sq cm, and 100 ma/sq cm. Polarization curves determined in this system were not significantly different from those obtained in the hydrogen fluoride-sodium fluoride system[3]. The gaseous products were nitrous oxide and nitrogen dioxide. The current equivalent of the anodic weight loss as 6.7 ma/sq cm, a value close to that obtained during the electrolysis of hydrogen fluoride-sodium fluoride[1].

In all the experiments presented here nitrous oxide was a major cathodic product. Cathode potentials monitored during electrolyses at 10 ma/sq cm and 50 ma/sq cm were about 1.5 and 2.5 volts, respectively.

Discussion

The anodic polarization curves determined in the hydrogen fluoride-nitric oxide system (Fig. 1) are similar to typical passivity curves which are determined by setting the current and measuring the resulting anode potential[2]. The region of negative resistance (metastable region) commonly associated with such curves can be determined only by potentiostatic methods. It is proposed that region A (Fig. 1) corresponds to the active region of the passivity curve while region B (Fig. 1) represents complete passivity. This is confirmed by the following experimental observations: prolonged electrolysis exclusively at currents in region B did not result in metal attack, while prolonged electrolysis in region A caused severe metal dissolution.

The onset of passivity was appreciably delayed at currents in region B when the anode was first pre-activated in region A. Electrolysis at low current density (region A) produced a thick, nonadherent deposit of nickel fluoride on the anode. This treatment must have activated the metal surface because, on increasing the currents to those prevailing in region B, the anodic potentials observed were less than would result if a clean nickel electrode was used.

Electrochemical explorations (Fig. 4) revealed conclusively that the surface condition of nickel was the determining factor in establishing the anode potential for a given current density. During the period of this experiment there were no significant changes in the concentration or in the resistance of the solution that could provide alternative explanations for the potential behavior. Figure 4 indicates that once passivity is accomplished, the potential does not revert to its active value when currents in region A are applied.

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The electrolytic products of interest, nitroxy fluoride and oxygen difluoride, represented only a few percent of the total current passed. It was shown, however, that oxygen fluoride formed exclusively at the passive nickel surface. In contrast, deliberate activation of the surface, either by preactivation in region A, or by using the current reversal technique, resulted in the formation of nitroxy fluoride.

Electrolysis in the hydrogen fluoride-sodium fluoride-nitric oxide system did not result in the production of either oxygen difluoride or nitroxy fluoride. The polarization phenomena and the equivalent current for metal dissolution in this system were indistinguishable from the hydrogen fluoride-sodium fluoride system. It is therefore concluded that the formation of oxygen difluoride or nitroxy fluoride did not result from the discharge of fluoride ions to form fluorine.

It appears that the onset of passivity in hydrogen fluoride is affected by the strength of the oxidizing agent present. Thus, with dinitrogen tetroxide (a stronger oxidizing agent than nitric oxide) present[1], passivity resulted on the application of a relatively low current in comparison to the hydrogen fluoride-nitric oxide system where relatively high currents were required.

The strength of the oxidizing agent is related to its effectiveness as a cathodic depolarizer. Comparison of the results of three systems, hydrogen fluoride-dinitrogen tetroxide, hydrogen fluoride-nitric acid, and hydrogen fluoride-nitric oxide, confirmed that the above listing of systems is in order of decreasing oxidizing strength. The open circuit potential of nickel was of the order 0.4 volt anodic to the platinum electrode in all three systems. In hydrogen fluoride-dinitrogen

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tetroxide electrolytes, cathodic polarization was small, less than 1 volt vs the platinum reference electrode at 100 ma/sq cm. After electrolysis for over an hour at this current density, cathode potentials were greater than 1 volt and minor quantities of nitrous oxide were produced.

In the hydrogen fluoride-nitric acid system, the cathode potentials at 10 ma/sq cm and 100 ma/sq cm were about 1 and 2 volts, respectively. Under these conditions more nitrous oxide was found than in the former system. In the hydrogen fluoride-nitric oxide system, the cathode potentials at 10 ma/sq cm and 50 ma/sq cm were of the order of 1.5 and 2.5 volts, respectively. Electrolysis in this system at 50 ma/sq cm resulted in an appreciable yield of nitrous oxide. It is concluded that the polarization characteristics of the cathode in the three systems are related to the strength of the oxidizing agent present.

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Footnotes

1. S. Evans, H. H. Rogers, and J. H. Johnson; "The Hydrogen Fluoride-
   Dinitrogen Tetroxide System," submitted for publication.

2. M. Stern, J.Electrochem. Soc., 105, 638 (1958).

3. H. H. Rogers, S. Evans, and J. H. Johnson; "The Hydrogen Fluoride-
   Nitrous Oxide System," submitted for publication.

4. H. H. Rogers, S. Evans, and J. H. Johnson; "The Electrolytic Drying
   of Hydrogen Fluoride," submitted for publication.

Acknowledgement
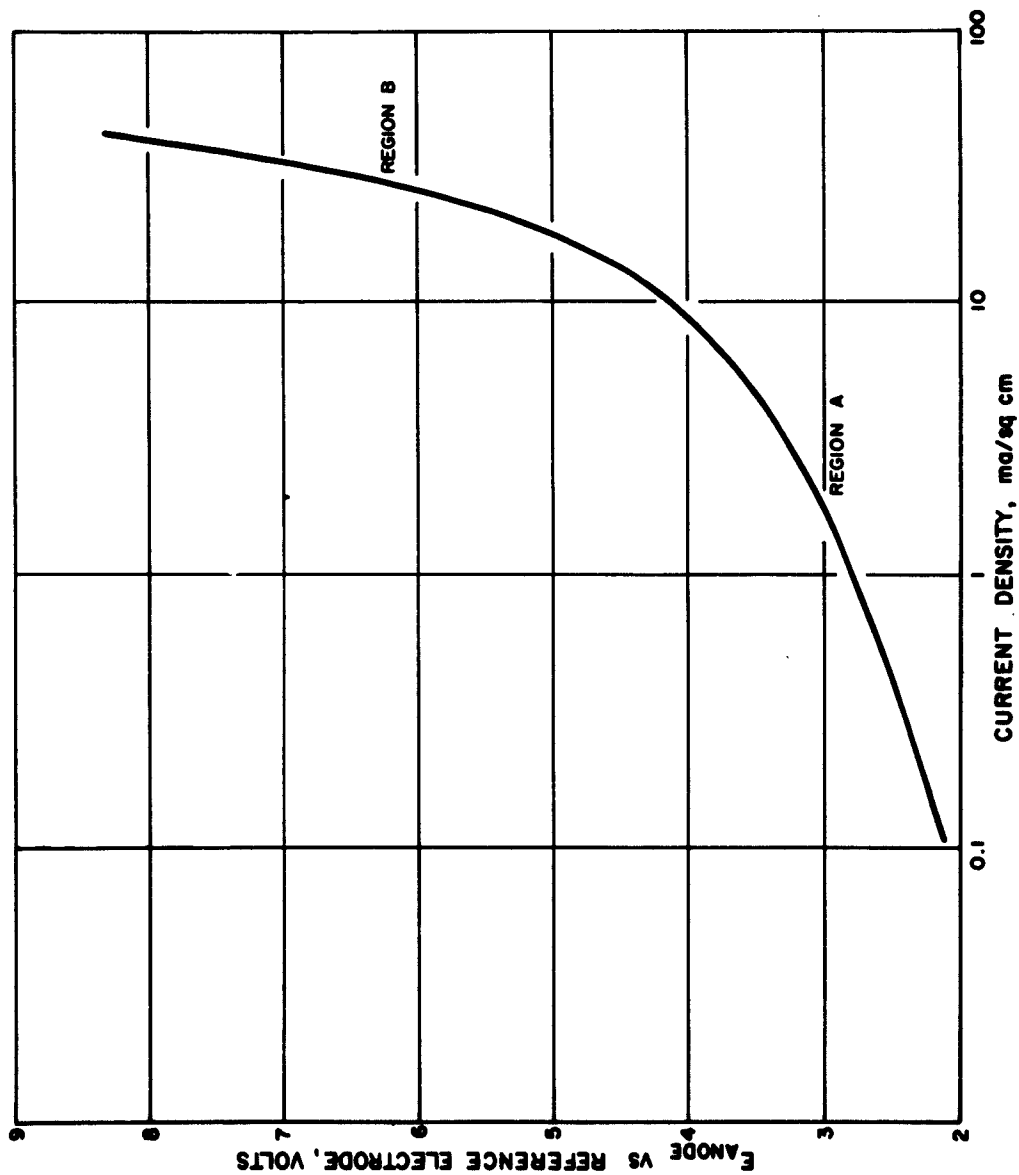
Figure 1. Typical Anodic Polarization Curve Obtained on Nickel in Hydrogen
Fluoride-Nitric Oxide Solution
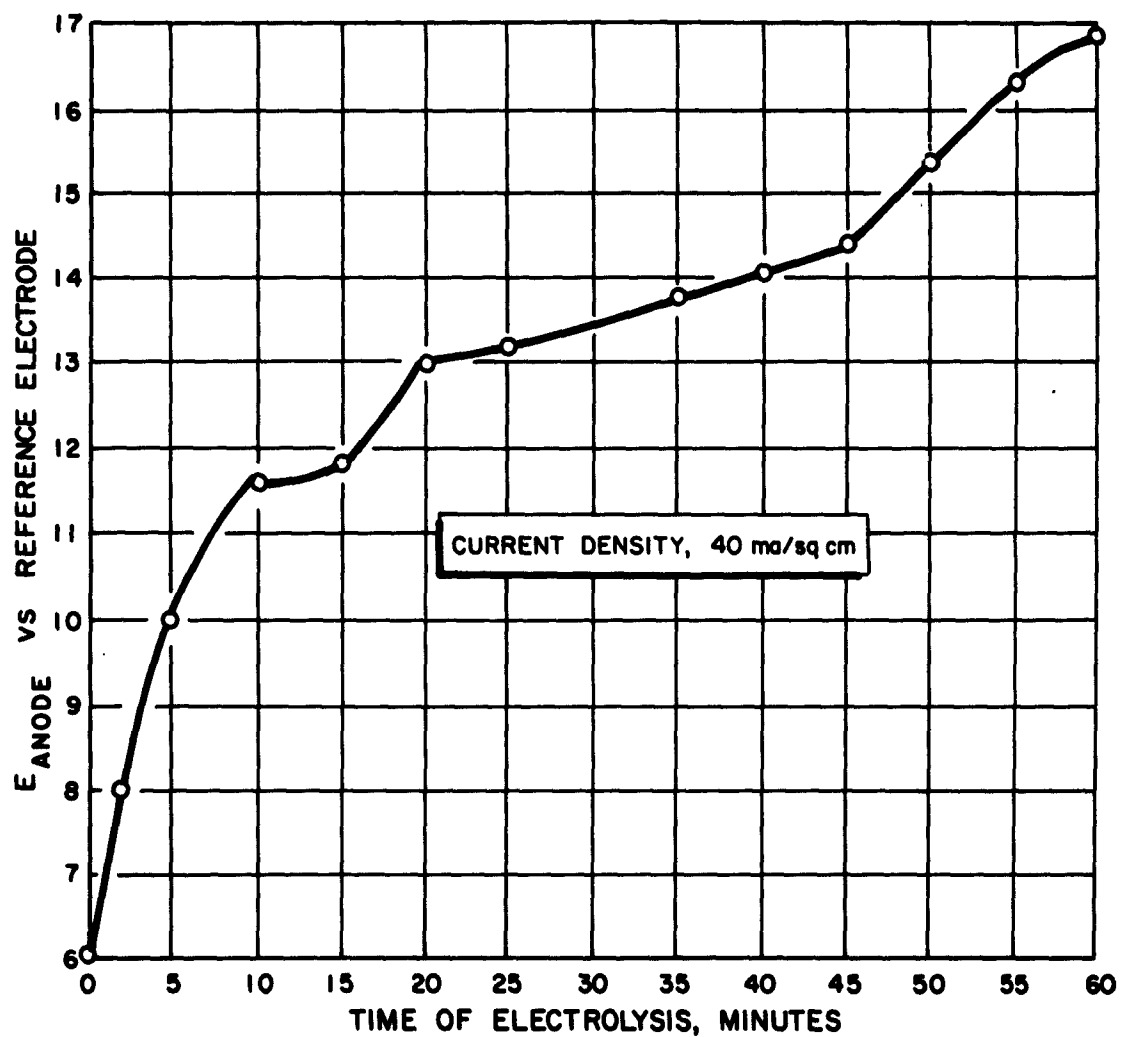
Figure 2.   Anode Potential as a Function of Time on
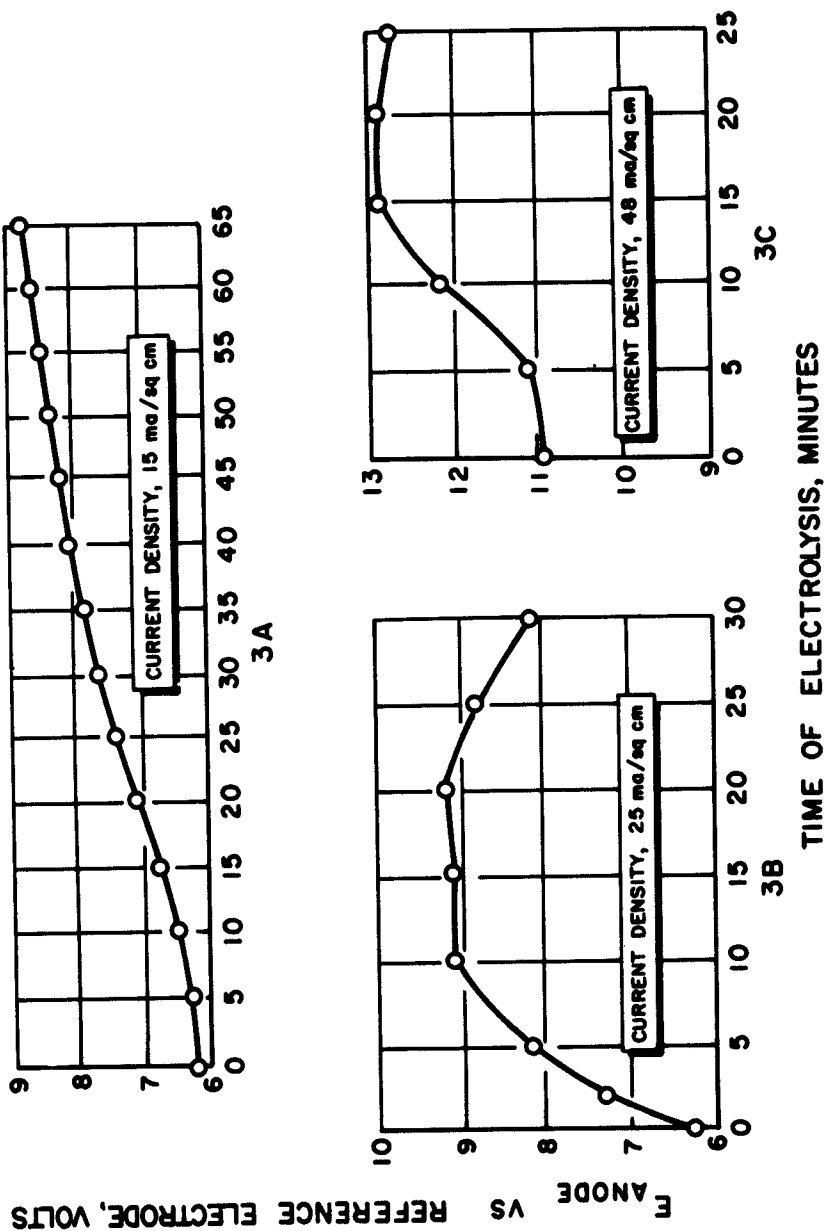Electrolysis at 40 ma/sq cm
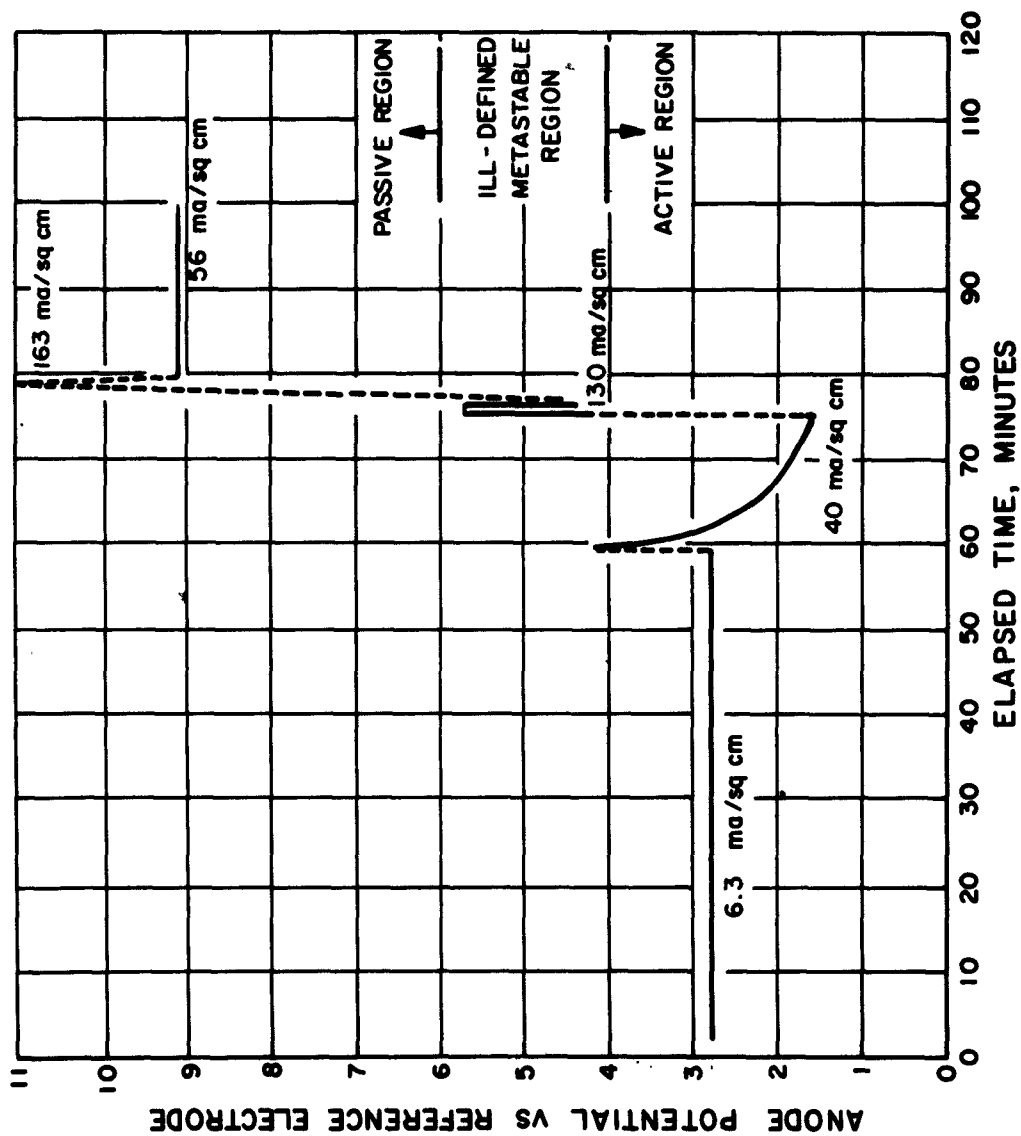
Figure 3. Anode Potential vs Time of Electrolysis

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Figure 4. Anode Potential as a Result of Treatment at Various Current Densities

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WIDE RANGE CURRENT REGULATOR

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A current regulator operating over a continuous
range of 0.0006 to 15 amperes has been developed.
At high currents, the regulation of the output
current with a change in load resistance from
maximum to zero was 0.5 percent while at low
currents regulation was 0.2 percent. The effect
of heat accumulation and of input voltage changes
on output current are also reported. A very simple
current regulator operating in the microampere
region is also described.

List of Figures

INTRODUCTION

This paper describes a current regulator which was designed as a constant current supply for an electrolytic cell used for electrochemical synthesis in anhydrous hydrogen fluoride. The circuitry and performance of the regulator, which operates over a current range greater than four orders of magnitude, are described.

The basic principles of the regulator can be described in terms of a common base amplifier[1] or a common emitter amplifier with feedback[2]. (1-2) Since the explanations in the above references and other literature are adequate no attempt will be made to repeat them here.

BASIC CIRCUIT

The basic circuit (Fig. 1) is capable of superb performance at low (Fig. 1) current levels and has been used in electrochemical studies in this laboratory. For example, with a planar 2N697 for Q_1, R_1 = 3KΩ, R_2 = 300KΩ, and B_2 = 6 volts, the regulator operated over a range of 20 to 1800μa. At the 500μa level, the maximum variation in current was $\pm$0.05 percent with a change in output voltage from 0 to 6 volts. The circuit will operate at lower current levels if a low leakage transistor such as 2N1613, 2N2102, or 2N2219 is selected and resistors R_1 and R_2 are changed to the appropriate values. The 2N697 is capable of operation to 30 volts (output),

1. Application Note 4B, "Current Regulator," Delco Radio Division, General Motors Corp., Kokomo, Ind.

2. Application Note AN3, "Current Regulator," Minneapolis-Honeywell Regulator Co., Minneapolis 8, Minnesota

3. Military Standardization Handbook, "Selected Semiconductor Circuits," MIL-HDBK-215, June 15, 1960, Superintendent of Documents, U. S. Government Printing Office, Washington 25, D.C.

while a 2N1893 will permit operation to 90 volts. Higher current operation is possible, especially if a higher power device unit such as a 2N2270 or 2N2102 is mounted on a small heat sink.

Temperature sensitivity of the base-emitter junction potential which causes a drift in the regulated current is an undesirable feature of the basic curcuit. Specifically the drift of the base-emitter potential is about 2 mv/° C which is equivalent to a 2% change in output current for a 60° rise in junction temperature. If stability is an important consideration the power dissipated in the transistor must be kept low, making the circuit suitable for low current regulation only.

It would be desirable to reduce the voltage of B_1 to reduce, in turn, the power dissipated in R_1 and R_2. For example, at a regulated current of 10 amperes, the power dissipated in R_1 and R_2 is about 50 watts. If B_1 were to be reduced to 2 volts, thereby reducing the power lost in R_1 and R_2 to about 10 watts, the resultant drift in current caused by the temperature coefficient of V_{BE} would be 10%. This point is covered as part of the over-all problem of regulator design discussed below.

COMPOUND CONNECTION OF TRANSISTORS

The degree of current regulation obtained in the basic current regulator (Fig. 1) is dependent upon the transconductance $(\Delta I_C / \Delta V_{BE})$ conductance is generally increased[2] by the use of the Darlington compound connection (Fig. 2a) which, however, retains the thermal problems   (Fig. 2a)

associated with the basic circuit. Experimentally, the thermal drift
was found to be excessive (Fig. 3). The complementary Darlington circuit   (Fig. 3)
(Fig. 2b) presents an almost ideal solution as can be seen from a plot   (Fig. 2b)
of the experimental results (Fig. 3). In this complementary configuration,
the base-emitter junction of the power transistor which is subject to
heating is separated from that part of the circuit which determines the
magnitude of current flow. The small amount of drift which remained was
undoubtedly a result of the trace of heat dissipated by the 2N1613. If
an additional transistor is needed to increase regulator performance
further, it can be used in a conventional Darlington connection with the
power transistor, 2N1138A. Their base-emitter junctions would not be in
the reference loop and, therefore, would not cause additional drift.

    A further advantage of the separation of the main current handling
loop from the reference loop, is the small change in base-emitter voltage
of the control transistor with collector current, compared to the very
large change in base-emitter voltage of the power transistor with
collector current. The current regulation of this complementary con-
figuration is, therefore, inherently better. For example, a typical
15-ampere power transistor will increase its base-emitter voltage 0.6
volts as the collector current is increased from 1 to 10 amperes. In
contrast, a typical silicon planar transistor (control transistor) would
experience a change in base-emitter voltage of about 0.1 volt for a
collector current change from 1 to 10 ma.

WIDE RANGE CURRENT REGULATOR

This regulator was designed to operate over a range of currents from a low of 0.6 milliampere to a high of 15 amperes. The circuit (Fig. 4) is based on the complementary Darlington configuration with appropriate switching and controls to permit operation over the desired current ranges. The settings of the switches and rheostats for the various ranges are listed in Table I.

Circuit Description

The reference voltage is obtained by using three silicon diodes, D_2, D_3, and D_4 as voltage regulators. These diodes and the NPN input transistor, Q_1, were mounted on a separate chassis to avoid thermal drift resulting from the heat dissipated by the rheostats. The 4.7 volt Zener diode, D_1, and the pilot lamps were used to obtain a relatively constant current through the reference diodes, even though the input voltage varied over a range from 3 to 33 volts. The two germanium power transistors, Q_2 and Q_3, were mounted on the same heat sink. When particularly high power levels were encountered, a small blower was used to cool the heat sink. Alternately, parallel transistors with small emitter resistors can be added to Q_3 to permit greater power dissipation. In actual operation, only rarely was the use of the blower necessary, because the input voltage was generally adjusted to reduce the voltage drop through the regulator to the minimum required by the application, thereby preventing excessive dissipation in Q_3.

(Fig. 4)

TABLE I

CONTROLS, WIDE RANGE CURRENT REGULATOR

Range, Amperes	Switch Positions			Adjustment, Rheostats		
	S_1	S_2	S_3	R_2	R_3	R_4
0.0006-0.07	A	A	B	Fine		Coarse
0.07-1.3	A	A	A	Coarse	Fine	
1.3-8	B	A	A	Fine	Coarse	
7.5-15	B	B	A	Fine	Coarse	

Components

Details of some of the components are presented in Table II. The
devices underlined were used to obtain the test data. The other devices
listed, or any semiconductor having equivalent characteristics, can be
substituted with similar results. It is important, however, to select a
low leakage transistor for Q_2 and a transistor with low thermal resistance
for Q_3. High gain transistors for Q_2 and particularly Q_3 will give
better current regulation than will low gain units.

The switches should be high quality units capable of carrying the
maximum current to be controlled with low contact resistance. Any
change in contact resistance will, of course, cause a corresponding
change in output current. With rheostats R_2 and R_3, there was a
significant contact resistance problem. After a period of operation, an
accumulation of dirt (mostly graphite) caused a high resistance connection
with a resultant drastic change in output current. Cleaning of the
brushes and windings proved to be only a temporary solution. A suggestion
by the manufacturer of the rheostat that silver brushes be substituted for
the graphite—metal composition brushes, was followed with good results.

Performance

The performance of the wide range current regulator is apparent
from Figure 5. For example, in the lower current ranges, the change in
output current caused by a corresponding change in load resistance from
maximum to zero ohms was found to be 0.2%. In the higher current ranges,
a current change of 0.5% was found under equivalent conditions. The
maximum voltage at which the regulated output current was available was
increased by raising the input voltage. The maximum permissible input
voltage was limited only by transistor and pilot lamp voltage ratings.

TABLE II

COMPONENTS, WIDE RANGE CURRENT REGULATOR

R_1 - Set for I_{max} = 1.3 amps, on 0.07 to 1.3 amp. range

R_5 - Length of No. 16 Nichrome, cut for I_{min} = 7.5 amps on 7.5 to 15 amp. range

D_1 - 1N1519 or <u>1N1589</u>

D_{2-4}- 1N456 or <u>1N482</u>

Q_1 - 2N697 (Pianar), <u>2N1613</u>, 2N2219, 2N2270

Q_2 - <u>2N539</u>, 2N553, 2N1971, 2N2139, 2N2143

Q_3 - <u>2N2081</u>, 2N2153, 2N2157, 2N2491

The drift of the output current as a function of time was found to be less than 1% at the end of a 15-minute period. Test conditions were $I = 7.2$ amperes, $E_{in} = 10$ volts, and $E_{out} = 0$ volts (short circuited output). The initial heat-sink temperature was 25° which rose to 63° after 15 minutes. In another test ($I = 3.0$ amperes, $E_{in} = 15$ volts, and $E_{out} = 7$ volts) the drift was less than 1% at the end of a 120-hour period.

The change in output current caused by a change in input voltage was also investigated. A change of 0.3% was observed for a 10% change in input voltage. Initial test conditions were $I = 10$ amperes, $E_{in} = 11$ volts, and $E_{out} = 5$ volts.

The change in output current caused by a change in ambient temperature has not been considered because this regulator was designed for use in laboratories where only moderate ambient temperature excursions are expected. If large ambient temperature changes are to be a factor in design then a temperature-compensated reference loop would be needed.

OTHER CURRENT REGULATOR DESIGNS

The principles of the current regulator based on the complementary Darlington configuration are applicable to regulators operating at current and voltage levels other than the circuits given. For high current operation power dissipation rather than current handling capability becomes the controlling factor. Therefore, it is necessary to parallel several output transistors to achieve operation at 60 amperes, for example. It should be pointed out that the use of several parallel power transistors reduces the total drive requirements because the current gain of a germanium power transistor is normally higher at moderate current levels. Operation of a regulator at voltage levels up

to at least 160 volts is readily achieved because of the availability of alloy-diffused germanium power transistors. Again, power dissipation is a very important factor in design.

ACKNOWLEDGEMENT

REFERENCES

1. Application Note 4B, "Current Regulator," Delco Radio Division, General Motors Corp., Kokomo, Indiana

2. Application Note AN3, "Current Regulator," Minneapolis-Honeywell Regulator Co., Minneapolis 8, Minnesota

3. Military Standardization Handbook, "Selected Semiconductor Circuits," MIL-HDBK-215, June 15, 1960, Superintendent of Documents, U.S. Government Printing Office, Washington 25, D.C.
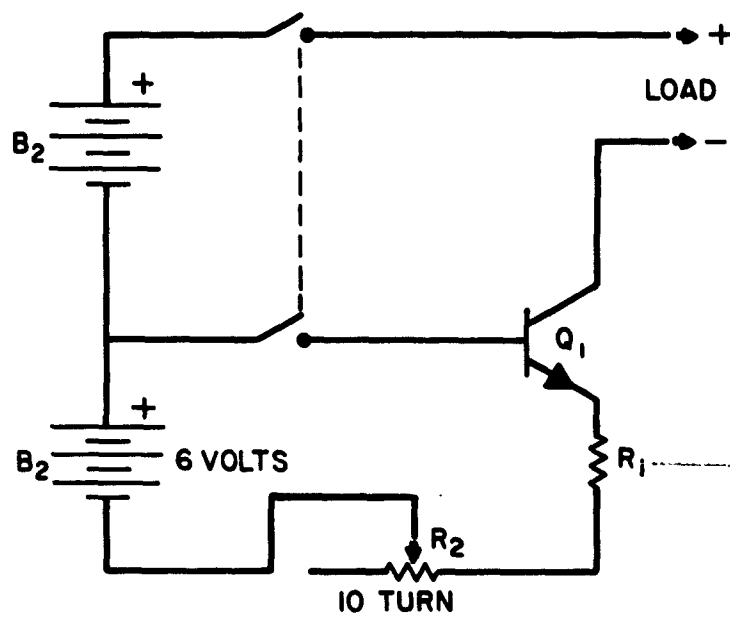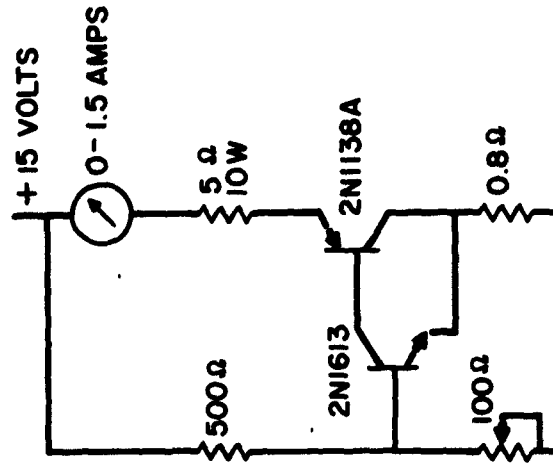
Figure 1. Basic Circuit

11
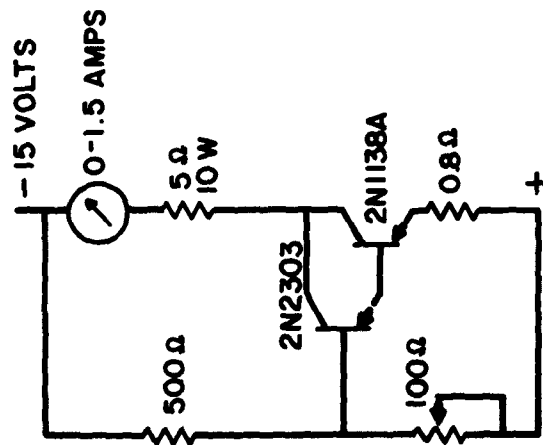
B. COMPLEMENTARY DARLINGTON

A. DARLINGTON

h_{FE} OF 2N1613 AND 2N2303 MATCHED TO $\pm$ 5 PERCENT
2N1138A MOUNTED ON $4\frac{3}{4}$ X 4 X $\frac{1}{16}$ INCH ALUMINUM
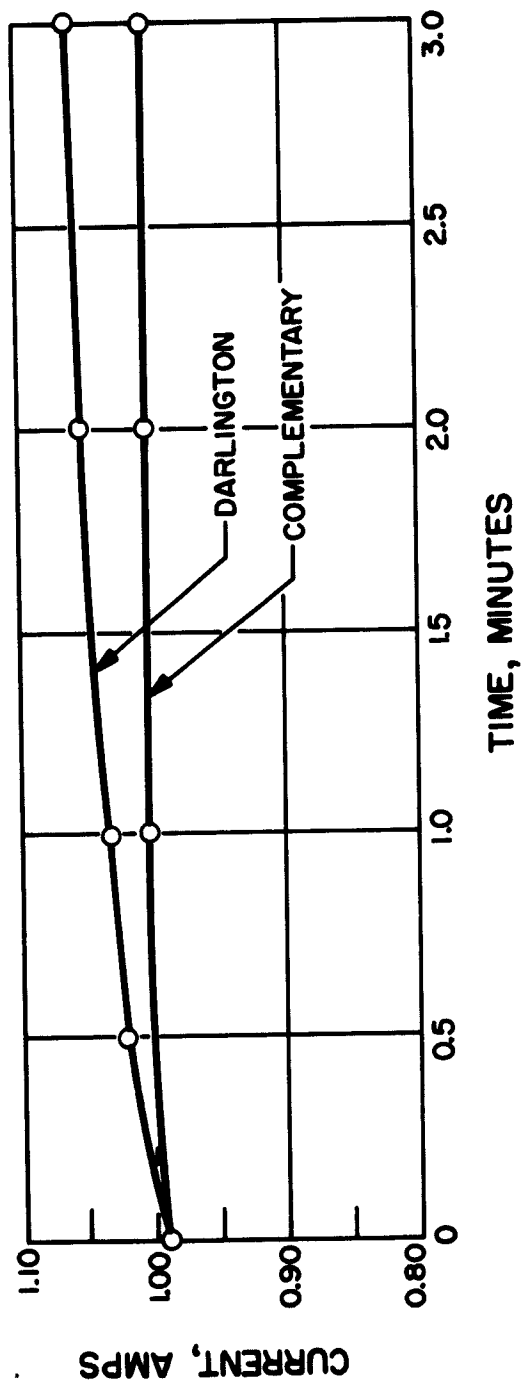
Figure 2. Circuit Configuration

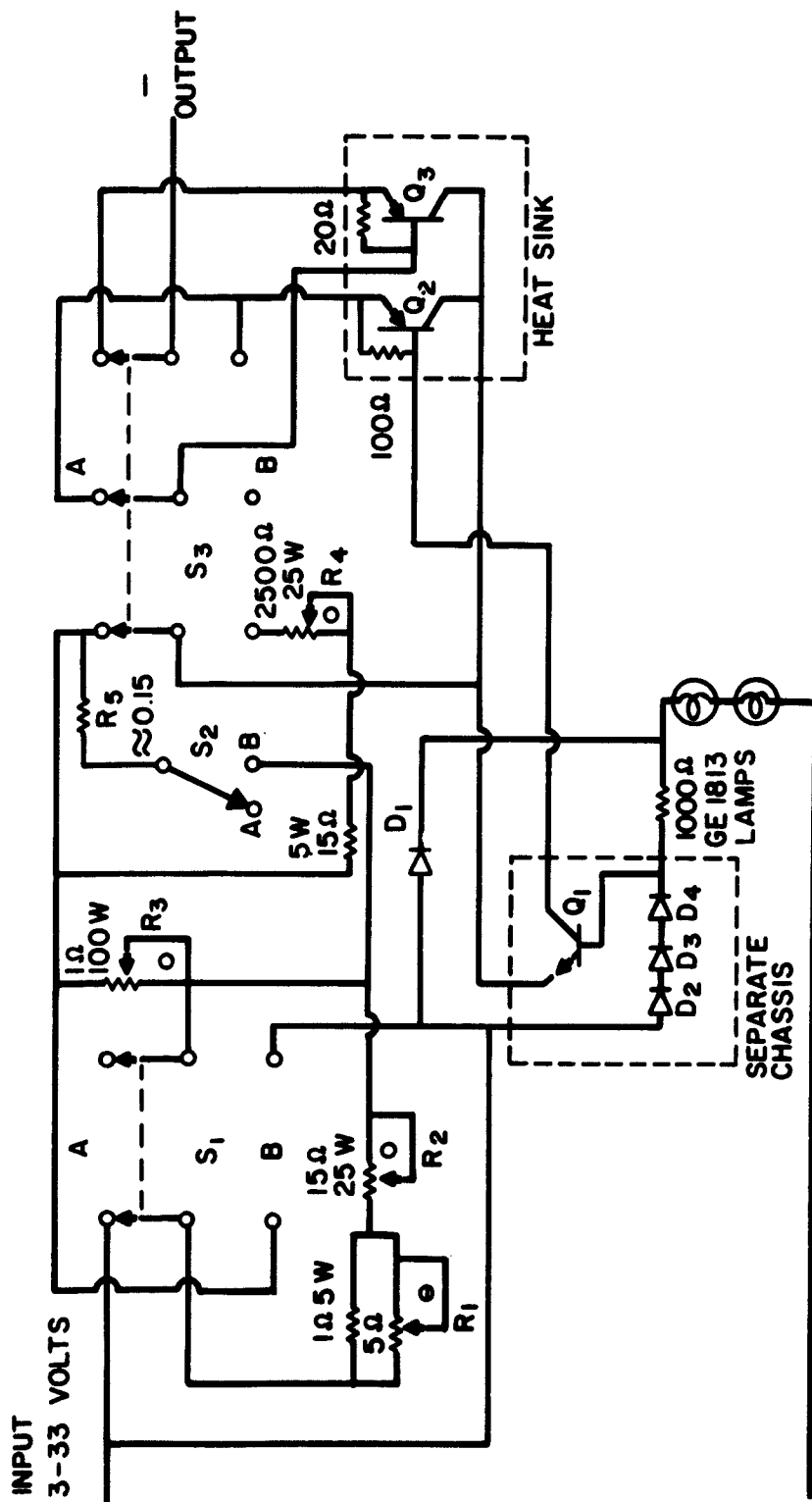Figure 3. Effect of Circuit Configuration on Drift
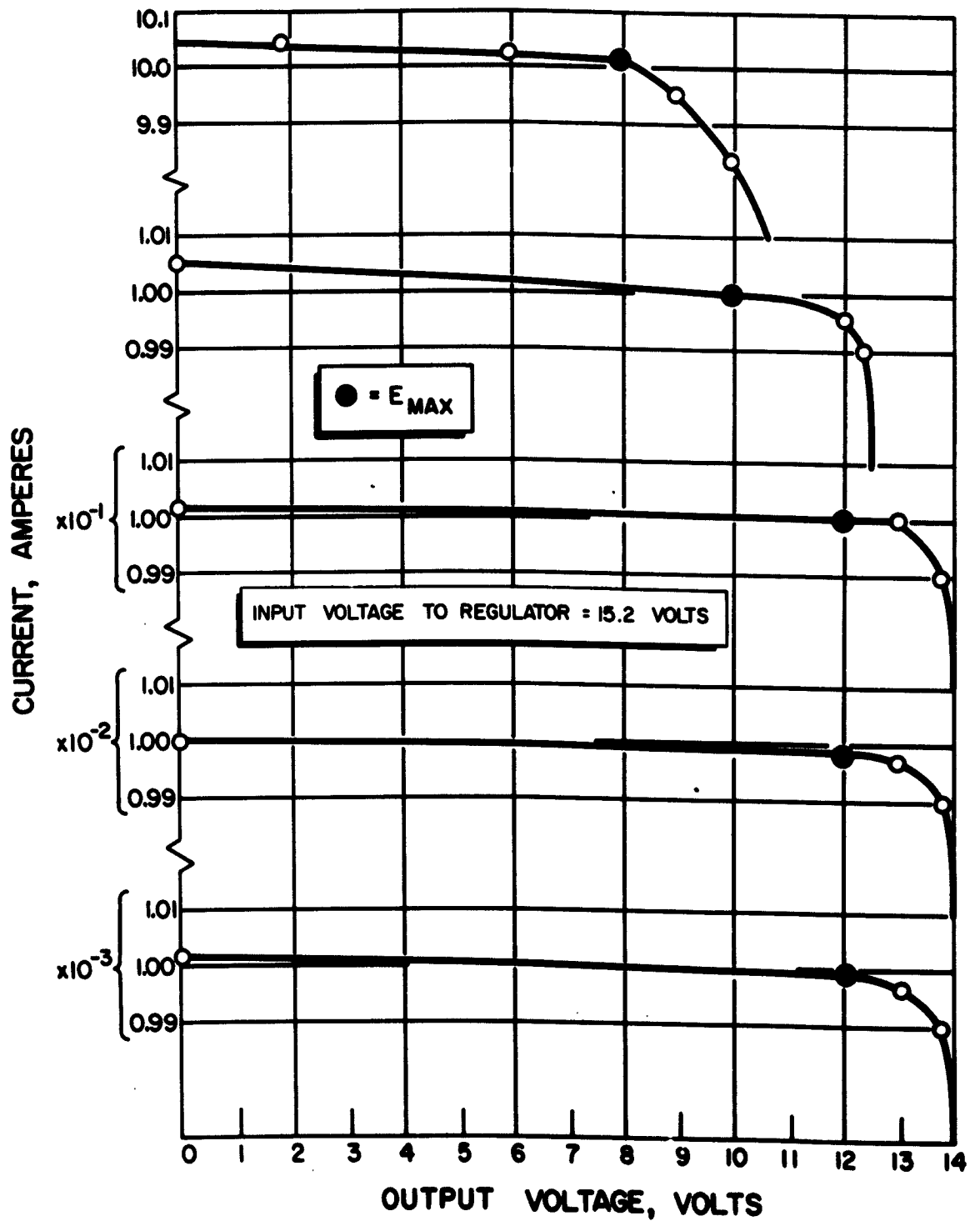
Figure 4. Wide Range Current Regulator

Figure 5. Wide Range Current Regulator Performance